WATER POLLUTION CONTROL RESEARCH SERIES • [illegible]

PB 205 824

Petrochemical Effluents Treatment Practices

DETAILED

Reproduced by
NATIONAL TECHNICAL
INFORMATION SERVICE
Springfield, Va. 22151

DEPARTMENT OF THE INTERIOR • FEDERAL WATER [illegible]

1 **Accession Number**

W 72-03299

2 **Subject Field & Group**

Ø5D

SELECTED WATER RESOURCES ABSTRACTS
INPUT TRANSACTION FORM

5 **Organization**

Engineering- Science, Inc./Texas, Austin, Texas

6 **Title**

PETROCHEMICAL EFFLUENTS TREATMENT PRACTICES, DETAILED Report,

10 **Author(s)**

Gloyna, Earnest F.
Ford, Davis L.

16 **Project Designation** FWPCA Contract No 14-12-461.
Program ~~No~~ 12020 --- 02/70,

21 **Note**

Available from the National
Technical Information Service
as PB 205824, $3.00 in
paper copy, $0.95 in microfiche

22 **Citation** Water Pollution Control Research Series, ~~No 12020 — 2/70~~ Feb 1970, 279 p, 37 fig, 46 tab, 301 ref, 2 append

23 **Descriptors (Starred First)**

*Oil, *Oil wastes, *Chemical wastes, Industrial wastes, Water analysis, Analytical Techniques, Sampling, Organic matter, Toxicity, Phenols, Odor, Color, Turbidity, Biochemical oxygen demand, Hydrogen ion concentration, Organic loading, *Water reuse, Research and development, Waste identification, Algae, *Waste water treatment

25 **Identifiers (Starred First)**

~~None~~

27 **Abstract**

500 new petroleum products are introduced on the market each year, making the petroleum industry and its allied petrochemical industries some of the nation's fastest growing industries. The petrochemical industry is projected as increasing by 9% per year through 1975. Most of the pollutional load from petrochemical industries emanates from process waste streams. ~~Much of this material is well documented, and~~ the processes for reducing its potential harm to the environment are well developed and understood. However, constant research and development efforts are continually introducing new pollutants into the environment. Therefore, development of new products should now include development of treatment schemes by which the wastes from the new products may be alleviated. Care must be exercised even in the sampling procedures, since many petroleum-based chemicals interfere with the accepted analytical test procedures. Finally, feasibility studies are needed to determine the capability of the petrochemical industries to re-use more of their wastewaters in the plant, and physical, chemical, and biological treatment are discussed. (Lowry-Texas)

(See also W 70-07511)

Abstractor Mark V. Lowry

Institution Texas Univ, Austin

SEND, WITH COPY OF DOCUMENT, TO: WATER RESOURCES SCIENTIFIC INFORMATION CEN
U.S. DEPARTMENT OF THE INTERIOR
WASHINGTON, D. C. 20240

WATER POLLUTION CONTROL RESEARCH SERIES

The Water Pollution Control Research Reports describe the results and progress in the control and abatement of pollution of our Nation's waters. They provide a central source of information on the research, development, and demonstration activities of the Federal Water Pollution Control Administration, Department of the Interior, through in-house research and grants and contracts with Federal, State, and local agencies, research institutions, and industrial organizations.

THE CHARACTERISTICS AND POLLUTIONAL PROBLEMS ASSOCIATED WITH PETROCHEMICAL WASTES

Detailed Report

Prepared by

ENGINEERING-SCIENCE, INC./TEXAS
Austin, Texas

Dr. Earnest F. Gloyna, Consultant
Dr. Davis L. Ford, Manager

for the

FEDERAL WATER POLLUTION CONTROL ADMINISTRATION

U. S. DEPARTMENT OF THE INTERIOR

Program No. 12020 Contract No. 14-12-461

February 1970

Copies of this report are available at the
Robert S. Kerr Water Research Center, P. O.
Box 1198, Ada, Oklahoma 74820

FWPCA Review Notice

This report has been reviewed by the Federal Water Pollution Control Administration and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the Federal Water Pollution Control Administration, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

ACKNOWLEDGMENTS

Appreciation is hereby expressed to the many contributors, reviewers, and editors who helped compile this report and insure its completeness and accuracy.

This profile was sponsored by the Federal Water Pollution Control Administration, U. S. Department of the Interior. The preliminary draft was reviewed on behalf of the Federal Water Pollution Control Administration by Mr. J. A. Horn, Mr. L. D. Lively, Mr. L. W. Muir, Mr. K. M. Mackenthun, Mr. Richard Duty, Mr. W. C. Schilling, and Mr. George Rey. Their comments and suggestions are duly acknowledged.

Members of the petrochemical industry also have been most cooperative in the review and editing of the report. These include Mr. R. D. Sadow of Monsanto Chemical Company, Mr. Sid O. Brady of Humble Oil and Refining Company, and Mr. R. D. Pruessner of Petro-Tex Chemical Company.

Particular appreciation is expressed to Dr. Lial F. Tischler, Dr. Carl E. Adams, and Dr. William Kwie who helped review the literature and compile the original manuscript.

BLANK PAGE

This report reviews various aspects of the petrochemical industry as related to pollution control. The areas reviewed cover the following topics:

TABLE OF CONTENTS

Page

ACKNOWLEDGMENTS i

TABLE OF CONTENTS ii

LIST OF TABLES ix

LIST OF FIGURES xii

RESEARCH NEEDS - CONCLUSIONS AND RECOMMENDATIONS xiv
- CHAPTER I xiv
- CHAPTER II xiv
- CHAPTER III xxiv
- CHAPTER IV xv
- CHAPTER V xv
- CHAPTER VI xvi
- CHAPTER VII xvii
- CHAPTER VIII xix

Chapter

I HISTORY OF THE PETROCHEMICAL INDUSTRY I-1
- PRE-WORLD WAR II I-1
- WORLD WAR II I-2
- POST WORLD WAR II I-2
  - Principal Products and Production Capacity I-2
  - Comparison With Entire Chemical Industry I-3
  - Geographical Location I-3
  - Water Use I-7
- REFERENCES I-11

II DESCRIPTION OF THE PETROCHEMICAL INDUSTRY II-1
- PRINCIPAL PETROCHEMICAL PRODUCTS AND INTERMEDIATES II-1

Page

Categorization of Products II-3
  Olefins II-3
  Aromatics II-8
  Paraffins II-10
  Miscellaneous Petrochemicals II-10
PROJECTED GROWTH OF THE PETROCHEMICAL INDUSTRY II-11
  Plastics and Resins II-14
  Synthetic Fibers II-15
  Synthetic Rubbers II-15
  Other Petrochemical Products and Intermediates II-15
  Effect of New Products on Growth II-16
REFERENCES II-17

III PETROLEUM RAW MATERIALS III-1
  NATURAL GAS III-1
  CRUDE PETROLEUM III-2
  REFINERY GASES III-3
  LIGHT TOPS III-3
  HEAVY FRACTIONS III-5
  AROMATICS FROM PETROLEUM III-5
  REFERENCES III-7

IV PETROCHEMICAL PROCESSES IV-1
  PRIMARY CONVERSION PROCESSES IV-1
    Distillation IV-1
    Extraction IV-2
    Adsorption and Absorption IV-2
    Crystallization IV-2

Page

SECONDARY CONVERSION PROCESSES IV-3
  Oxidation IV-5
  Halogenation IV-9
  Nitration and Sulfonation IV-10
  Alkylation IV-11
  Dehydrogenation IV-12
  Polymerization IV-12
  Other Processes IV-13
PROCESSES AS WASTE SOURCES IV-14
  By-Product Formation IV-14
  Side-Product Formation IV-14
  Incomplete Reactions IV-14
  Mechanical and Accidental Losses IV-14
REFERENCES IV-24

V CHEMICAL AND PROCESS RELATED CLASSIFICATION OF WASTES V-1
COOLING WATER V-2
PROCESS EFFLUENTS V-2
  Solvent Processes V-3
  Caustic Washes V-3
  Acidic Wastes V-3
  Washing and Scrubbing Operations V-4
  Crude Petroleum Desalting V-4
  Other Sources V-4
CHEMICAL CLASSIFICATION OF PETROCHEMICAL WASTES V-4
  Inorganic Compounds V-5
    Metals V-5
    Non-metals V-5
  Organic Compounds V-7
    Hydrocarbons V-7
    Substituted Organic Compounds V-8

Page

a. organic acids and their salts V-8
b. alcohols V-9
c. aldehydes and ketones V-9
d. esters V-10
e. ethers V-10
f. halogenated hydrocarbons V-10
g. nitrogenated compounds V-11
h. phenolic compounds V-12
i. organic sulfur compounds V-12
Miscellaneous Organics V-14
REFERENCES V-15

VI WASTE POLLUTIONAL EFFECTS AND THEIR CHARACTERIZATION VI-1
EFFECTS OF POLLUTION ON RECEIVING WATER VI-1
Aesthetic Effects VI-1
Biological Effects VI-2
Miscellaneous Effects VI-9
EFFECTS OF POLLUTION ON WATER USE AND REUSE VI-10
Water Quality for In-Plant Reuse VI-10
Cooling Water VI-10
Process Waters VI-10
Water Quality Required for Other Users VI-12
Agriculture Uses VI-12
Industrial Uses VI-12
Effects on Water Treatment Processes VI-12
Effects on Groundwater VI-14
PHYSIOLOGICAL EFFECTS OF PETROCHEMICAL WASTES VI-14
Taste and Odor VI-16
Toxicity VI-19
Toxicity to Microorganisms VI-21
Fish Toxicity VI-22

Page

CONVENTIONAL POLLUTIONAL PARAMETERS VI-34
  Acidity VI-35
  Alkalinity VI-35
  Color and Turbidity VI-44
  pH VI-44
  Organic Material VI-45
    Biochemical Oxygen Demand VI-45
    Chemical Oxygen Demand VI-50
    Total Organic Carbon VI-51
  Total Oxygen Demand VI-51
  Immediate Oxygen Demand VI-52
  Solids VI-52
  Surface Activity VI-52
  Taste and Odor VI-53
  Temperature VI-53
  Toxicity VI-54
  Oils VI-54
  Miscellaneous Pollutant Parameters VI-54
    Phenols VI-54
    Inorganic Ions VI-54
    Volatility VI-55
    Heavy Metals VI-55
  Total Plant Effluent Analysis VI-55
IDENTIFICATION AND MONITORING METHODS VI-56
  Chemical Methods of Analysis VI-56
    Inorganic Chemicals VI-56
    Organic Chemicals VI-58
  Biological Methods VI-63
REFERENCES VI-68

VII TREATMENT AND CONTROL OF PETROCHEMICAL WASTES VII-1

	Page
REDUCTION OF WASTE LOADS BY INTERNAL IMPROVEMENTS	VII-1
Reduction of Raw Material Losses	VII-1
Recovery of Usable Reaction Products	VII-2
Process Modifications	VII-7
Water Reuse	VII-8
In-Plant Control	VII-10
Waste Stream Segregation	VII-10
PHYSICAL TREATMENT PROCESSES	VII-11
Gravity Separation	VII-11
Oil Separation	VII-11
Sedimentation	VII-16
Stripping Processes	VII-20
Solvent Extraction	VII-23
Adsorption	VII-25
Combustion	VII-26
Filtration	VII-30
Miscellaneous Treatment Methods	VII-30
CHEMICAL TREATMENT METHODS	VII-33
Neutralization and pH Adjustment	VII-33
Coagulation - Precipitation	VII-39
Oxidation Processes	VII-42
Miscellaneous Methods	VII-51
BIOLOGICAL TREATMENT PROCESSES	VII-51
General Considerations	VII-51
Biodegradability	VII-51
Nutrients	VII-55
Neutralization Requirements	VII-56
Equalization	VII-57
Pre- and/or Primary Treatment	VII-58
Temperature	VII-58

Page

Activated Sludge Processes VII-61
Trickling Filter Processes VII-69
Aerated Lagoons VII-70
Waste Stabilization Ponds VII-74
Miscellaneous Biological Treatment Processes VII-78
Multiple Biological Treatment Schemes VII-78
OTHER METHODS OF DISPOSAL VII-81
Dilution VII-81
Discharge Into Municipal Sewerage Systems VII-85
Deep Well Disposal VII-85
Ocean Outfall VII-86
Submerged Combustion VII-91
Incineration of Liquid Wastes VII-91
REFERENCES VII-93

VIII ECONOMIC ASPECTS OF PETROCHEMICAL WASTE TREATMENT VIII-1
THE COST OF WASTE TREATMENT VIII-1
Primary Treatment VIII-2
Biological Treatment Processes VIII-2
Tertiary Treatment Processes VIII-10
Ion Exchange VIII-10
Carbon Adsorption VIII-21
Sludge Handling and Disposal VIII-21
Ultimate Disposal VIII-21
RETURNS TO THE PETROCHEMICAL INDUSTRY VIII-21
REFERENCES VIII-27

APPENDIX I - PROCESS INFORMATION
A - Primary Petrochemicals
B - Common Intermediates
C - Third-Generation Petrochemicals
APPENDIX II - Major Petrochemical Products and Wastes Profile

LIST OF TABLES

Table	Title	Page
II-1	PRINCIPAL ETHYLENE-BASED PRODUCTS	II-9
II-2	PROJECTION OF UNITED STATES PETROCHEMICAL PRODUCTION CAPACITY FOR SELECTED CHEMICALS	II-12
IV-1	PETROCHEMICAL PROCESSES AS WASTE SOURCES	IV-15
IV-2	CALCULATION OF HYDROCARBON LOSSES FROM PROCESS EQUIPMENT IN AN ETHYLENE PLANT	IV-21
VI-1	FIVE-DAY BOD VALUES FOR SOME PURE ORGANIC COMPOUNDS OFTEN FOUND IN PETROCHEMICAL PLANTS	VI-4
VI-2	LETHAL TEMPERATURES FOR SOME SELECTED FISH SPECIES	VI-8
VI-3	SOLUBILITY OF COMMON SALTS	VI-11
VI-4	WATER QUALITY FOR SELECTED AGRICULTURE USES	VI-13
VI-5	ORGANIC CHEMICAL POLLUTANTS IDENTIFIED IN GROUNDWATER	VI-15
VI-6	DETECTABLE CONCENTRATIONS OF SOME PETROCHEMICAL COMPOUNDS CAUSING TASTE AND ODOR IN WATER	VI-17
VI-7	SOME ORGANIC CHEMICALS CAUSING ADVERSE TASTES IN FISH	VI-20
VI-8	TOXICITY OF SOME SELECTED PETROCHEMICALS TO _CHLORELLA_ _PYRENOIDOSA_	VI-23
VI-9	TOXICITY BIOASSAY RESULTS	VI-26
VI-10	TYPICAL WASTE CHARACTERISTICS OF PRIMARY CONVERSION AND REFINING PROCESSES	VI-36
VI-11	TYPICAL SPENT CAUSTIC STREAM CHARACTERISTICS	VI-37
VI-12	TYPICAL ACID WASTE CHARACTERISTICS	VI-38
VI-13	TYPICAL PROCESS WASTE CHARACTERISTICS - MISCELLANEOUS	VI-40
VI-14	TYPICAL WASH WATER CHARACTERISTICS (SCRUBBING PROCESSES)	VI-43

Table	Title	Page
VI-15	TOTAL PLANT EFFLUENT ANALYSES	VI-47
VII-1	USABLE SIDE-PRODUCTS FROM SOME TYPICAL PETROCHEMICAL PROCESSES	VII-5
VII-2	SPECIFIC APPLICATIONS OF OIL SEPARATORS IN THE PETROCHEMICAL INDUSTRY	VII-12
VII-3	TYPICAL EFFICIENCIES OF OIL SEPARATION UNITS	VII-15
VII-4	SEDIMENTATION OF SOME PETROCHEMICAL WASTES	VII-18
VII-5	PERFORMANCE AND OPERATING CHARACTERISTICS OF FLOTATION UNITS TREATING PETROCHEMICAL WASTES	VII-19
VII-6	AVERAGE OPERATING CHARACTERISTICS OF SOUR WATER STRIPPERS	VII-21
VII-7	SOLVENTS USED TO EXTRACT PHENOLS FROM WASTEWATER	VII-24
VII-8	DESTRUCTION OF PETROCHEMICAL WASTES BY COMBUSTION METHODS	VII-27
VII-9	TYPICAL FILTRATION APPLICATIONS IN PETROCHEMICAL WASTE TREATMENT	VII-31
VII-10	TYPICAL APPLICATIONS OF NEUTRALIZATION OF pH ADJUSTMENT TO PETROCHEMICAL WASTES	VII-35
VII-11	COAGULATION AND SEDIMENTATION OF PETROCHEMICAL WASTES	VII-40
VII-12	OXIDATION PROCESSES USED IN PETROCHEMICAL WASTE TREATMENT	VII-43
VII-13	DESIGN AND EFFICIENCY OF SOME SULFIDE OXIDATION UNITS	VII-46
VII-14	OZONATION OF SYNTHETIC RUBBER PROCESS WASTES	VII-50
VII-15	RELATIVE BIODEGRADABILITY OF CERTAIN ORGANIC COMPOUNDS	VII-53
VII-16	WASTEWATER CHARACTERISTICS REQUIRED FOR OPTIMUM BIOLOGICAL TREATMENT	VII-59
VII-17	ACTIVATED SLUDGE TREATMENT OF PETROCHEMICAL WASTES	VII-65
VII-18	TRICKLING FILTER TREATMENT OF PETROCHEMICAL WASTES	VII-71

Table	Title	Page
VII-19	AERATED LAGOON TREATMENT OF PETROCHEMICAL WASTES	VII-75
VII-20	WASTE STABILIZATION PONDS	VII-77
VII-21	MISCELLANEOUS BIOLOGICAL TREATMENT PROCESSES FOR PETROCHEMICAL WASTES	VII-79
VII-22	MULTIPLE BIOLOGICAL TREATMENT SYSTEMS FOR PETROCHEMICAL WASTES	VII-82
VII-23	PETROCHEMICAL WASTE DISPOSAL BY DEEP WELL INJECTION	VII-87
VII-24	POLLUTANTS REQUIRING SURFACE TREATMENT PRIOR TO DEEP WELL INJECTION	VII-90
VII-25	TYPES OF WASTE TREATMENT USED IN THE PETROCHEMICAL AND CHEMICAL INDUSTRIES	VII-92
VIII-1	SUGGESTED BASIS FOR COSTING UNIT PROCESSES	VIII-3
VIII-2	OPERATING COSTS - WASTE TREATMENT PLANTS	VIII-17

LIST OF FIGURES

Figure	Title	Page
I-1	PETROCHEMICAL END-USES	I-4
I-2	PRODUCTION OF ORGANIC CHEMICALS IN THE UNITED STATES	I-5
I-3	LOCATION OF HYDROCARBON PROCESSING PLANTS	I-6
I-4	TOTAL WATER INTAKE FOR CHEMICAL AND ALLIED PRODUCTS INDUSTRY	I-9
I-5	CLASSIFICATION OF WATER USED BY THE PETROCHEMICAL INDUSTRY	I-10
II-1	FIRST-GENERATION PETROCHEMICALS	II-2
II-2	PRINCIPAL PRODUCT DERIVATIVES FROM THE OLEFINS	II-4
II-3	PRINCIPAL PRODUCT DERIVATIVES FROM THE AROMATICS	II-5
II-4	PRINCIPAL PRODUCT DERIVATIVES FROM THE PARAFFINS	II-6
II-5	PRINCIPAL PRODUCT DERIVATIVES FROM VARIOUS SOURCES	II-7
III-1	PRIMARY DISTILLATION OF CRUDE PETROLEUM	III-4
IV-1	PRIMARY CONVERSION PROCESSES	IV-4
IV-2	SECONDARY CONVERSION PROCESSES	IV-6
V-1	SOLUBILITY OF PHENOLS IN WATER	V-13
VI-1	SCHEME FOR IDENTIFICATION OF TRACE ORGANICS	VI-64
VII-1	CAUSTIC REGENERATION PROCESSES	VII-4
VII-2	SPENT CAUSTIC NEUTRALIZATION	VII-38
VII-3	SULFIDE OXIDATION UNIT	VII-47
VII-4	TEMPERATURE EFFECT ON COD REMOVAL	VII-60
VII-5	PARAMETER RESPONSE TO ORGANIC LOADING	VII-63
VII-6	BIOLOGICAL TREATMENT IN A COOLING TOWER	VII-80
VIII-1	CAPITAL COST RELATIONSHIP - EQUALIZATION	VIII-6
VIII-2	CAPITAL COST RELATIONSHIP - NEUTRALIZATION	VIII-7
VIII-3	CAPITAL COST RELATIONSHIP - OIL SEPARATION	VIII-8
VIII-4	CAPITAL COST RELATIONSHIP - PRIMARY SEDIMENTATION	VIII-9

Figure	Title	Page
VIII-5	CAPITAL COST RELATIONSHIP - LAGOONS	VIII-11
VIII-6	CAPITAL COST RELATIONSHIP - AERATED LAGOON	VIII-12
VIII-7	CAPITAL COST RELATIONSHIP - ACTIVATED SLUDGE	VIII-13
VIII-8	CAPITAL COST RELATIONSHIP - MECHANICAL SURFACE AERATORS	VIII-14
VIII-9	CAPITAL COST RELATIONSHIP - FINAL CLARIFIER	VIII-15
VIII-10	CAPITAL COST RELATIONSHIP - TRICKLING FILTERS	VIII-16
VIII-11	CAPITAL COST RELATIONSHIP - ION EXCHANGE	VIII-19
VIII-12	CAPITAL COST RELATIONSHIP - CARBON ADSORPTION	VIII-20
VIII-13	CAPITAL COST RELATIONSHIP - FLOTATION THICKENING	VIII-23
VIII-14	CAPITAL COST RELATIONSHIP - VACUUM FILTRATION	VIII-24
VIII-15	CAPITAL COST RELATIONSHIP - TOTAL SLUDGE DISPOSAL	VIII-25
VIII-16	CAPITAL COST RELATIONSHIP - INCINERATION	VIII-26

RESEARCH NEEDS - CONCLUSIONS AND RECOMMENDATIONS

CHAPTER I:

It is concluded that the petrochemical industry will continue to grow and diversify. The chemical and allied products industry is expected to increase from the present 5.5 billion gallons per year to 23 billion gallons per year by year 2000. The production and sales of organic chemicals is expected to increase from the present production of 135 billion pounds per year to 200 billion pounds per year by year 1973. The petrochemical industry is projected to increase nine percent per year through 1975. Water use patterns have changed: in 1954 and 1962, respectively, cooling water requirements were 82 percent to 65 percent of the total water use. The industrial growth rates by geographical areas through 1975 will be 25, 15, and 10 percent, respectively, for the Pacific Coast and Alaska areas, Gulf Coast area, and Southeast, Puerto Rico and Virgin Islands area.

It is recommended that an updated profile of this industry be made every five years. Particular emphasis should be directed to the water use and reuse patterns for the newer petrochemical processes; advanced methods of waste handling; changes in water quality criteria for updated processes; and changes in industrial growth patterns.

CHAPTER II:

It is concluded that new products will be developed from existing "intermediate" petrochemicals, but also new petroleum-based derivatives will be developed to a greater extent. In 1955, the total petrochemical production constituted 24 percent, by weight, of the total chemical production. It is expected that the percentage will increase to 41 percent by 1970. It is anticipated that ethylene, an important petrochemical intermediate, will double (14 to 25 million metric tons annually) over the 1970 to 80 decade. Estimates indicate that about 500 new petroleum products are introduced to the market every year.

It is recommended that each of the major processes developed by the industry be studied with the objective of evaluating the trends in plant locations, effects on area-wide water quality, and treatment requirements.

CHAPTER III:

It is concluded that there will be no significant changes in petrochemical feedstocks, although the increasing demand for ethylene and butylene has required the petrochemical industry to look for additional sources of base material. Heavy fractions such as fuel oils are finding an increasing market as the source for these two olefins and other primary petrochemicals.

It is recommended that the patterns of feedstock usage be monitored and major changes be evaluated in terms of the water use and water reuse requirements, potential pollution problems, and product development.

CHAPTER IV:

It is concluded that the main contribution to environmental pollution from the petrochemical industry at present eminates from process waste streams. However, the principal processes and characteristics of their wastewaters are fairly well understood. The ranges of the waste volumes and organic concentrations vary considerably. Within the same process at different plant sites, the pollutant loads may range by more than one order of magnitude. Typically the reaction efficiency in the petrochemical industry has a wide variation. This efficiency may range from 60 percent to nearly 100 percent. Although the feedstock is recycled in the case of low conversion efficiency, the practice is highly dependent on market conditions. In addition to produce losses, there are mechanical losses and waste streams that contain side-products.

It is recommended that comparative cost analyses be made on several typical recycle (feedstock) practices and on associated wastewater treatment requirements, establishing a basis for optimizing the overall plant operations. First, comparative studies need to be made on a computerized model basis where operating variables can be generated and the results studied in detail. Second, a series of field studies should be made to test the model data and demonstrate the interrelationships of product handling with wastewater treatment costs.

CHAPTER V:

It is concluded that many of the conventional parameters, as compared to those developed for characterizing domestic wastewaters, do not adequately define the potential pollution characteristics of petrochemical wastes. In many cases the pertinent characteristics of a waste stream were ignored, the analytical procedures were inadequate for such complex wastes, and much of the reported data have been misinterpreted. Significant inconsistencies have been found in the measurement of organic carbon, including oil and oil-like substances; oxygen demand of compounds, as measured both chemically and biochemically; toxicity as reflected in both microbial and higher forms of plant and animal life, including man; interferences between petrochemical process waste constituents and reagents used in conventionally-accepted organic and inorganic characterization analyses; and availability of nutrients.

It is recommended that a comprehensive and coordinated evaluation program be developed specifically for standardizing the characterization techniques of wastewaters containing complex and undefinable petrochemical and related wastewater constituents. Such a program should include a correlation and interpretation of reported data and unpublished but available industrial data. Currently, an evaluation must be made of newly developed analytical techniques in comparison with conventional procedures. Finally, a thorough study must be made on the adaptability of newly developed parameters for governmental and industrial use. The latter study would involve an evaluation of the adaptability of newly developed parameters to (a) uniform nation-wide reporting practices, (b) national monitoring networks, (c) pollution or stream assimilation models (mathematical), and (d) on-stream and continuous monitoring systems.

CHAPTER VI:

It is concluded that petrochemical wastes may provide potential pollutants in the form of concentrated oxygen-demanding organic and inorganic materials, organic compounds not amenable to biological degradation, oil and oil-like substances, volatile and non-volatile suspended materials, color contributing solutions, toxic fractions, compounds responsible for taste and odors, heat, floatables and polymeric products, and agents which interfere with conventional analytical techniques and increasing problems in the treatment of heated waters.

Furthermore, it is concluded that much of these wastewaters could be reused within the plants with varying degrees of treatment.

It is recommended that long-term tests be conducted to evaluate the effects of intermediate and product waste streams on (a) aerobic and anaerobic biological degradation rates; (b) toxicity of these wastes on acclimated microbiological cultures, and both micro- and macro-plants and animals; (c) speciation and diversity index evaluations below selected plant sites.

It is further recommended that a serious evaluation be made on the treatment required for in-plant reuse and cost analyses be established on treatment for plant reuse and on treatment for discharge.

It is recommended that a series of studies be initiated to standardize the evaluation of the potential pollutional characteristics of all cooling tower and boiler water preparations, as well as their effects on waste treatment systems.

A detailed evaluation should be made at an early date of all the chemical interferences affecting the BOD and COD tests. Carefully controlled tests should be conducted to establish the BOD_5/BOD_u ratio.

It is additionally recommended that many of the more prevalent petrochemical compounds be analyzed in terms of unit weight of BOD, COD, TOC, and IOD per unit weight of the compound. A similar representation per unit weight of suspended solids discharged from various related processes would be of value.

Special properties of selected waste streams should be studied with respect to fish "tainting "(taste and odors in both fin fish and shell fish),induced changes in the surface activity of receiving waters, interaction of waste with chlorine and other waste treatment disinfectants, and effects of post polymerization on receiving waters.

Similarly, tests should be conducted to determine the effect of the more common process wastes on benthic organisms, selected plankton and acclimated biological cultures.

CHAPTER VII:

It is concluded that most of the wastewaters produced by the petrochemical industry require some form of primary product recovery and treatment, oil removal, settleable solids removal, and reduction in the organic content. By-product recovery possibilities represent a significant approach in reducing pollutants. There is much room for the use of in-plant separation of product and feedstock for recovery purposes.

It is further concluded that physical separation and disposal schemes have not been used as effectively as possible. For example, combustion procesesses are often overlooked as a potential disposal process, particularly when the wastes are too concentrated or too toxic for treatment by lower-cost biological methods. Stripping processes can be used more effectively throughout the petrochemical industry to remove volatile fractions from the collection of contaminated stream water runoffs.

Most wastewater from petrochemical plants contain wastes which are amenable to biological degradation. A significant group of these wastes exhibit a low biodegradation rate. Consequently, an optimal balance between physical, chemical, and biological treatment (with process modifications) must be considered in the development of a pollution abatement master plan.

For optimum wastewater management in the petrochemical industry, it is necessary to develop the wastewater treatment as an integral process of the overall plant. This necessitates the development of increased product and feedstock recovery, improved housekeeping, separation of non-contaminated wastes from waste streams, and separation of concentrated nonsoluble or otherwise solid fractions near each source.

Additionally, it is concluded that the master plan for in-plant wastewater collection should include facilities to segregate process waste from less contaminated streams. The latter falls in two categories: (a) those wastes derived from dry weather flows such as leaks from pumps, sample ports, packaging, container washings, kettle or batch operations; and (b) those wastewaters derived from wet weather runoffs. The containment and treatment of certain storm flows needs evaluation.

It is recommended that the following treatment and control evaluations be considered:

(a) physical treatment processes

1. The problem of oil-water and other emulsions should be studied, both with respect to influence on secondary biological waste treatment and the most efficient methods of breaking the emulsions, thus enhancing separation.

2. As the process streams are reused or recycled, the effluents will become increasingly warmer. Emphasis should be directed to evaluating methods of cooling various waste streams prior to subsequent treatment.

3. Many waste streams contain inorganic and organic solids which are difficult to remove (i.e., lime sludges containing heavy tars, oils, etc.). Physical separation processes in conjunction with coagulant aids, therefore, should be more thoroughly investigated.

(b) chemical treatment

1. The development of better techniques for evaluating the effects of various cooling tower and boiler water additives on secondary biological treatment and such analyses as may be affected adversely by these additives should be undertaken.

(c) biological treatment

1. An evaluation of the effect of various wastes on bio-flocculation, settling and all types of biological treatment systems is recommended. Specific attention should be directed to the toxic characteristics of these wastes.

2. The magnitude of biological reaction rates for major process wastes within the petrochemical industry should be estimated.

3. Methods of biological process modifications to maximize COD reduction should be considered.

4. A determination of the effects of various wastewaters on streams and brackish waters in terms of both biodegradation rates and reaeration rates should be made.

5. A more satisfactory way of evaluating
ents in brackish and salt waters should

6. The advantages (if any) of two-stage biological treatment versus single-stage biological treatment should be determined. Similarly, the advantages (if any) of tertiary treatment over other disposal means should be investigated.

7. The availability of complexed forms of nitrogen and phosphorus as a nutrient source to microorganisms in biological waste treatment plants should be evaluated.

(d) other methods of disposal

1. The technology by which persistent contaminants in benthic deposits can be studied should be developed.

2. Guidelines for the development of dilution thresholds for common petrochemical toxicants with respect to co-treatment with municipal wastes should be established.

CHAPTER VIII:

It is concluded that most waste streams from petrochemical plants will require some form of solids or oil separation, waste stream separation and pretreatment, and secondary biological treatment. The cost of this wastewater treatment can be reduced considerably by in-plant reuse of product waste streams and wastewater in general. Trends toward the co-treatment and joint treatment of industrial wastewaters necessitates the establishment of a formula for equitably prorating pollution control costs.

It is recommended that a detailed and basic study be initiated to evaluate the cost of treating wastes from single plants or process streams with combined wastes from several plants. The economy of scale in treating petrochemical wastes on an area-wide basis offers many advantages in dampening the effect of peak releases from individual processes, possibly neutralization, utilization and balance of nutrients, and more effective treatment supervision. However, the economy of scale is subject to geographical limitations. Conveyance costs may override any economy of scale inherent with regional type treatment concepts.

CHAPTER I

HISTORY OF THE PETROCHEMICAL INDUSTRY

The use of petroleum for the manufacture of chemical products is a relatively new addition to the chemical world. After the industry gained momentum to meet the demands of the Second World War, the growth rate continued to increase yearly. Modernized techniques and methods have been developed to locate and secure new sources of raw materials as the petroleum industry confronts the challenge of dwindling supplies. The history of this complex of industries is interesting and provides a foundation for understanding the fundamentals of the various operations involved.

PRE-WORLD WAR II

It appears that the first proposal to extract useful chemical derivatives from petroleum occurred in the late 19th century, but no chemicals of significance were produced until just prior to World War I. The first use of a petroleum fraction in a chemical process occurred in 1908 when the Germans used a gasoline fraction to prepare mononitrotoluene for dye production (Anon., Shell, 1966). This process was modified during the First World War to produce TNT.

The United States petrochemical industry had its inception in 1919 to 1920 as a result of research initiated during the war. In 1917, petroleum-derived propylene was used to produce acetone (Anon., Shell, 1966), but the first petrochemical produced in commercially significant quantities was isopropanol, developed by New Jersey Standard Oil Company in 1920 (Anon., Bus. Wk.,1960). The principal source of petrochemicals following World War I was refinery off-gases. These gases had traditionally been burned, but manufactures developed means for converting them to valuable chemical products.

Probably the most predominant feature of the period between the two world wars was the introduction of ethylene oxide derivatives into the chemical industry. Propylene was also used extensively in chemical manufacture, and butene was converted to ketones which were used in various solvents (Goldstein, 1958). Most of the products manufactured during this time were straight-chain aliphatic compounds. The manufacture of ammonia and nitrogeneous fertilizers using natural gas was also begun during this period (Anon., Shell, 1966). The petrochemical industry steadily increased in size during these years.

WORLD WAR II

The petrochemical industry gained great impetus as a result of the Second World War. When the war started the United State's supply of imported rubber was significantly reduced. Since there was an imperative need for synthetic rubber production the government was forced to spend $900 million in the construction of 30 major synthetic rubber plants using butadiene and styrene from 1940 to 1950 (Anon., Bus. Wk., 1960). Many other uses for petroleum hydrocarbons were developed during the war years; alcohols and synthetic detergents were manufactured from petroleum materials, and production of petroleum-based aromatics was initiated during this period. Previously, aromatics had primarily been produced from coal, and coke; aromatics obtained from petroleum rapidly replaced these other sources. Improved separation methods for other hydrocarbons added more petrochemicals to the list of products.

POST WORLD WAR II

Since World War II, the petrochemical industry has experienced a tremendous growth; production increased more than five times from 1945 to 1960. In 1960 the Department of Commerce listed more than 3,000 different petrochemical products (Anon., Bus. Wk., 1960) with organic chemicals constituting the major product of the industry. Petrochemical production increased from 1.0 million tons of product in 1945 to 11.5 million tons of product in 1963 (Anon., Shell, 1966). This rapid expansion continued, and 81 new projects were planned or are underway in the United States as of September, 1967 (Aalund, 1967).

Principal Products and Product Capacity

Organic chemicals are the chief product of the petrochemical industry; however, there are several inorganic petrochemicals which are manufactured in large quantities. Ammonia, sulfur, and carbon black are all important products. For example, the domestic output potential of ammonia as of September, 1967, was 17.3 million tons per year, an increase of 33 percent from 1966 (Aalund, 1967). The ammonia produced is used mainly in the manufacture of nitrogeneous fertilizers. Organic petrochemicals are used in a wide variety of products, including synthetic fibers, synthetic rubbers, plastics, resins, synthetic detergents, a variety of automotive chemicals, as well as numerous other products.

There has been a phenomenal growth of plastic production during the last decade. Polyethylene production was 2.6 billion pounds while polystyrene and vinyl production was much less than two billion pounds each in 1966 (Sawyer, 1966). Polyethylene is used in a variety of plastic products which include packaging materials for industrial and consumer goods; molded plastic products of all types; and some extruded plastics such as floor tiles, cable coverings, and hoses. Vinyls are used in surface coatings and many industrial plastic products, while polystyrenes are found in plastic foams and adhesives (Lewis, 1966). The increasing use of plastic both in industry and at home indicates that continued growth can be expected.

The production of synthetic rubber is another rapidly growing petrochemical industry. In 1966, synthetic rubber constituted 75 percent of the total rubber used in the United States (Sawyer, 1966). Similar figures were available for almost every petrochemical product, and growth predictions indicate that the industry will continue to expand at this rapid rate. Distribution of the many end-uses of petrochemicals is graphically illustrated in Figure I-1. Miscellaneous uses, which include synthetic detergents and industrial chemicals, are accounting for an increasing share of the total production capacity, and can be expected to increase in number as more chemicals are developed and new uses for existing chemicals are discovered.

Comparison With Entire Chemical Industry

There are several reasons for the rapid growth of the petrochemical industry, some of which include the expansion of industries which process petrochemicals into finished products, such as plastics and synthetic fibers; availability of cheap and abundant supplies of petroleum raw materials; low cost of producing petroleum-based chemicals as compared to production using non-petroleum sources; and increasing cost and limited supply of some non-petroleum raw materials (Stanley, 1963). The increase of petroleum-based stock in the production of organic chemicals is graphically depicted in Figure I-2. In 1963, more than 85 percent of the United States organic chemical production was petroleum-based as compared to only 56 percent in 1950.

Graphical Location

The locations of the major petrochemical plants in the United States are presented in Figure I-3, the majority of which are situated along the Gulf Coast between New Orleans, Louisiana, and Brownsville, Texas. This area contained approximately 80 percent of the nation's petrochemical production capacity in 1960. The two largest complexes, located at Beaumont and Houston, Texas, contribute 30 percent of total United States petrochemical output (Anon., Bus. Wk., 1960). Primary reasons for growth of the industry in this area include the availability of sea transport, location of 75 percent of United States petroleum reserves within easy reach, an abundance of fresh water required to meet the industrial demand, and the low cost of fuel available. Also, it is advisable for both economic and technical considerations to locate plants in close proximity since transferring chemicals from one plant site to another is common and usually done by pipeline. The Gulf Coast is a relatively flat area which makes pipeline construction economical. This region is now and should continue to be the center of petrochemical activity in the United States.

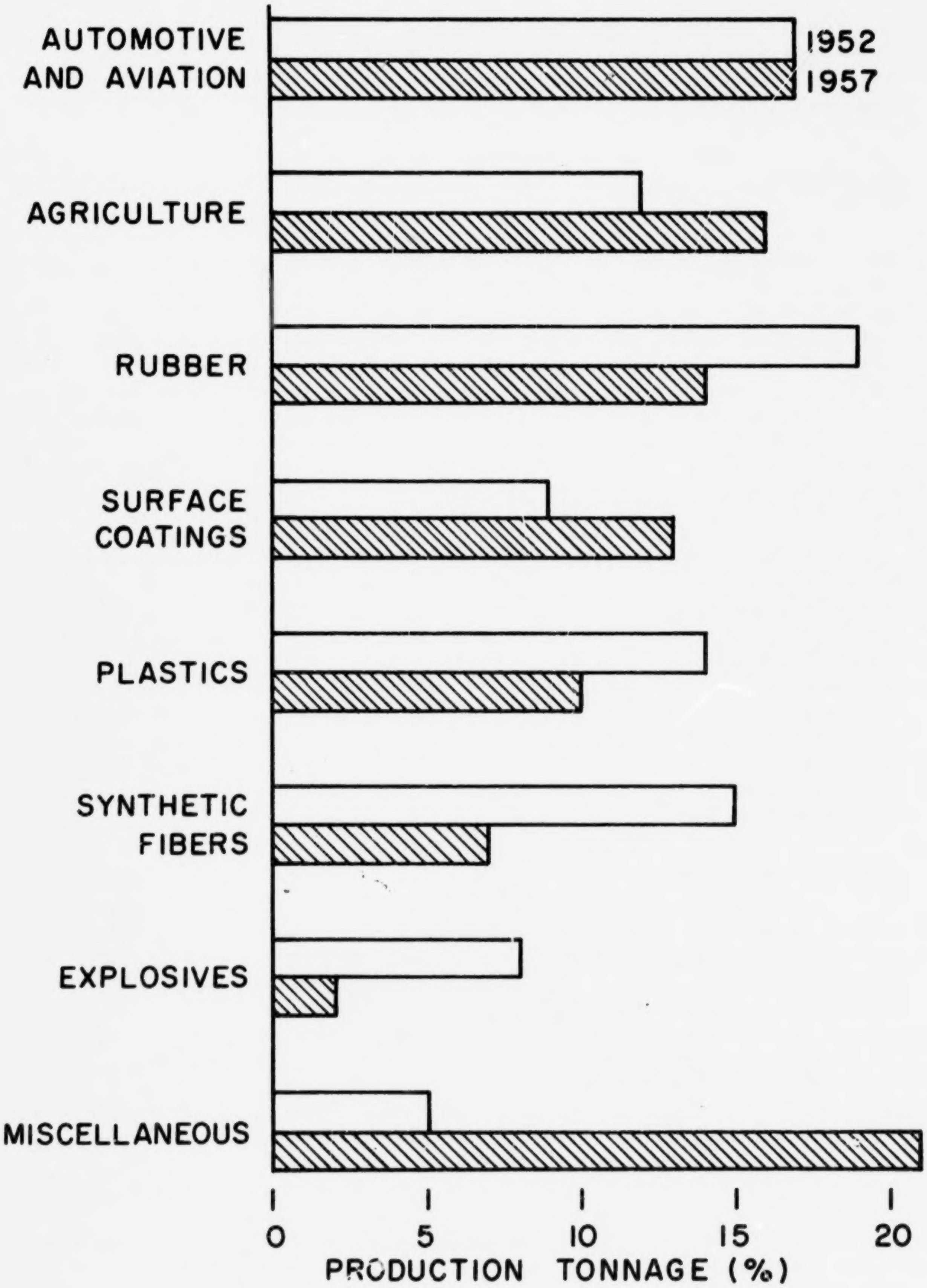


FIGURE I-1
PETROCHEMICAL END-USES
(Reference 7)

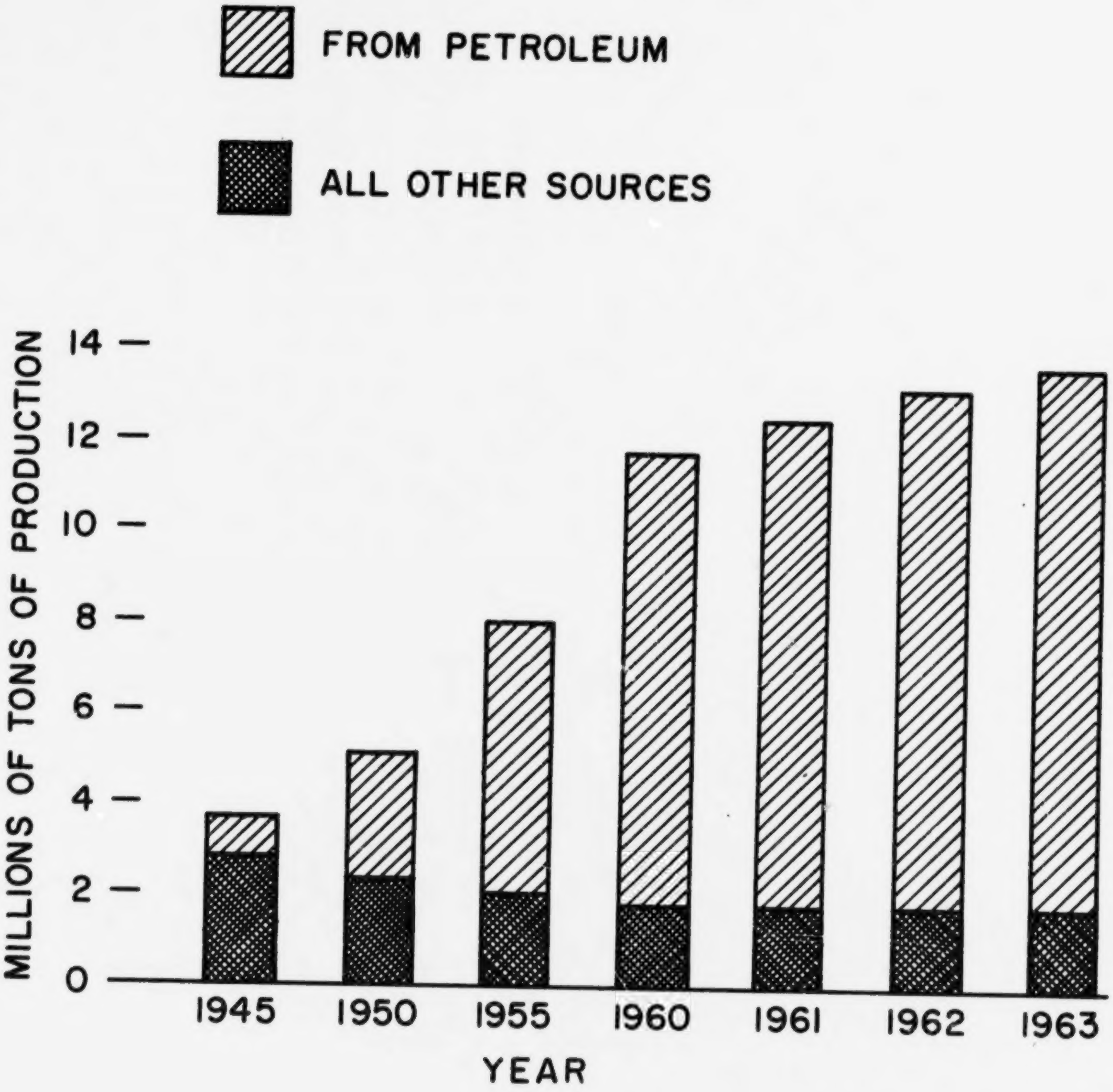


FIGURE I-2

PRODUCTION OF ORGANIC CHEMICALS IN THE UNITED STATES

(Reference 4)

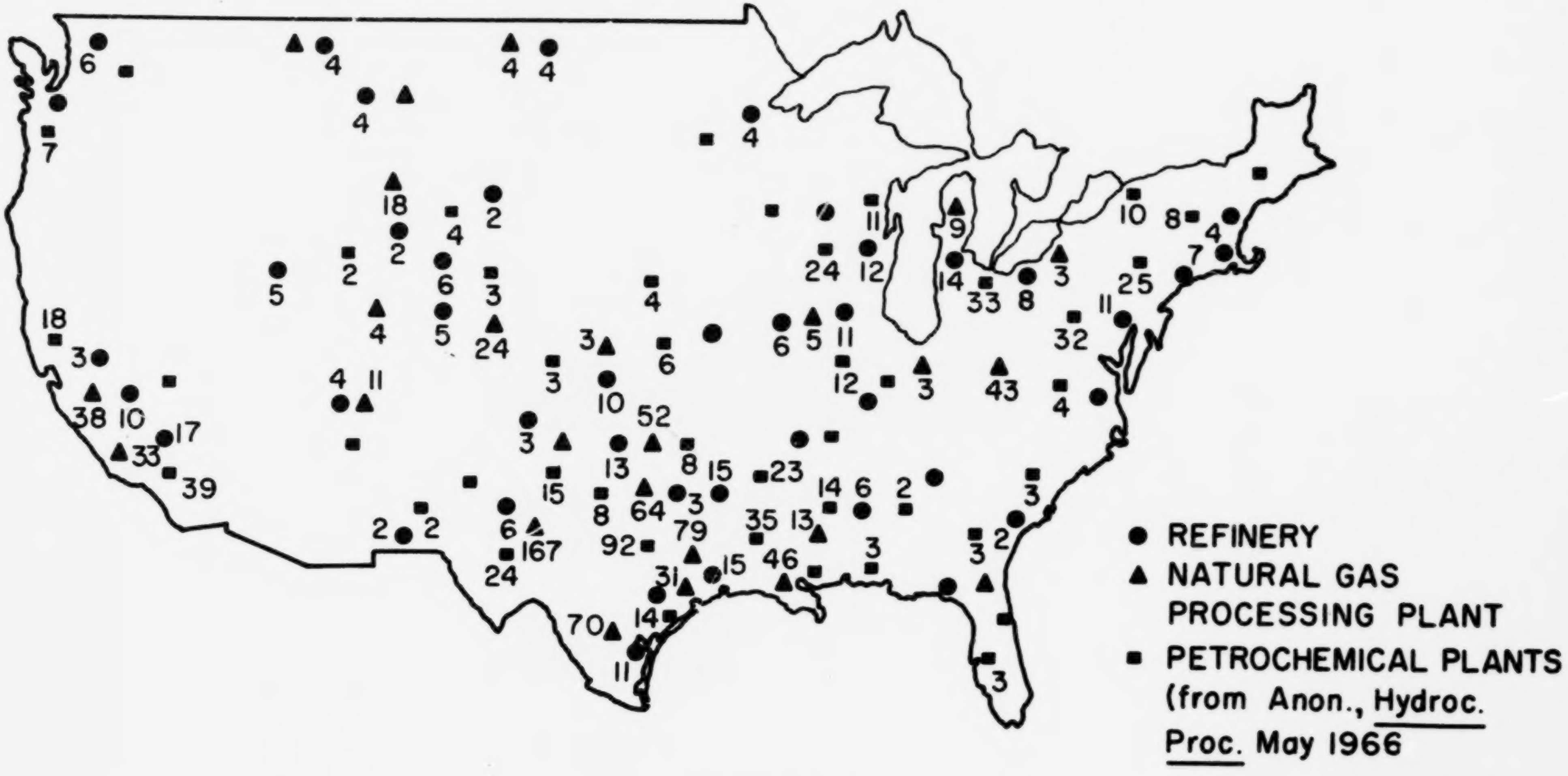

● REFINERY
▲ NATURAL GAS PROCESSING PLANT
■ PETROCHEMICAL PLANTS
(from Anon., Hydroc. Proc. May 1966

FIGURE I-3

LOCATION OF HYDROCARBON PROCESSING PLANTS

(Reference Anon., Hydroc. Proc., May 1966)

Water Use

Water use data for the petrochemical industry as distinguished from the total chemical industry is unaccomplished in the literature. However, historical data available from the chemical industry indicate that water intake increased an average of 45 percent during the decade from 1939 to 1949 (Anon., Water in Ind., 1950). These figures came from 154 plants which reported to the survey and represent increases in water use by each plant. This percentage increase does not include the water use requirements of new chemical plants constructed during this period. This represents a considerable quantity, probably much greater than the increase cited. The 1954 Census of Manufacturers showed that the chemical and allied products industry used 2,378 billion gallons of water per year. These data were obtained from the 1,164 plants which used 20 million gallons or more of water per year and constituted 95 percent of the water intake by the industry. Water reuse was practiced by 67 percent of these plants, and the gross water used was 4,032 billion gallons. The chemical industry utilized 83 percent of the water intake for cooling purposes, 9.5 percent as process water, and the balance for other miscellaneous purposes. The water used by the chemical industry represented 23.4 percent of the total industrial water use in 1954 (Senate Rept.No. 8.,1960).

The 1961 Census of Manufactureres indicated that in 1959 there were 933 chemical plants using 20 million gallons or more per year and their total water intake comprised 3,240 billion gallons per year. Some 74 percent of these plants reused their water, and the gross industrial water use by the chemical industry was 5,225 billion gallons per year. Approximately 66 percent of the water intake was consumed for cooling, a considerable drop from the 83 percent reported in 1954. Process water accounted for 14 percent and water used for generation of steam and electricity for 15 percent of the industry's water intake in 1959. Organic chemical production, which is predominantly petroleum-based, accounted for 44 percent of the annual water intake of the chemical industry.

Later water use data for the chemical industry was collected in 1962 (Anon., Water in Ind., 1965). This survey included 875 plants in the United States which employed approximately half of the total number of persons who worked for the chemical and allied products industries. These data should not be considered to represent the entire chemical industry since the definition of the industry by some includes packaging, blending, mixing, and distributing of chemical products, most of which use little or no water (Anon., Water in Ind., 1965). The total water withdrawal for these plants was 3,600 billion gallons in 1962. These plants reported using a total of 7,875 separate processes, 19 percent of which had no water-borne wastes. Water used for cooling constituted 65 percent of the water intake by the chemical industry in 1962.

The water intake by the chemical and allied products industries projected to the year 2000 is shown in Figure I-4. Actual water intakes for plants using 20 million gallons or more per year are plotted for 1954 and 1959. The projected data were obtained from a United States Senate Report, and those projections indicate that the chemical industry will be the number one industrial water consumer by the year 2000 (Senate Rept. No. 8.,1960). One-fifth of the industrial water demand in that year will have to be supplied in the Gulf Coast region since it will be the center of the chemical industry for reasons previously cited. The water use data presented above are summarized in Figure I-5.

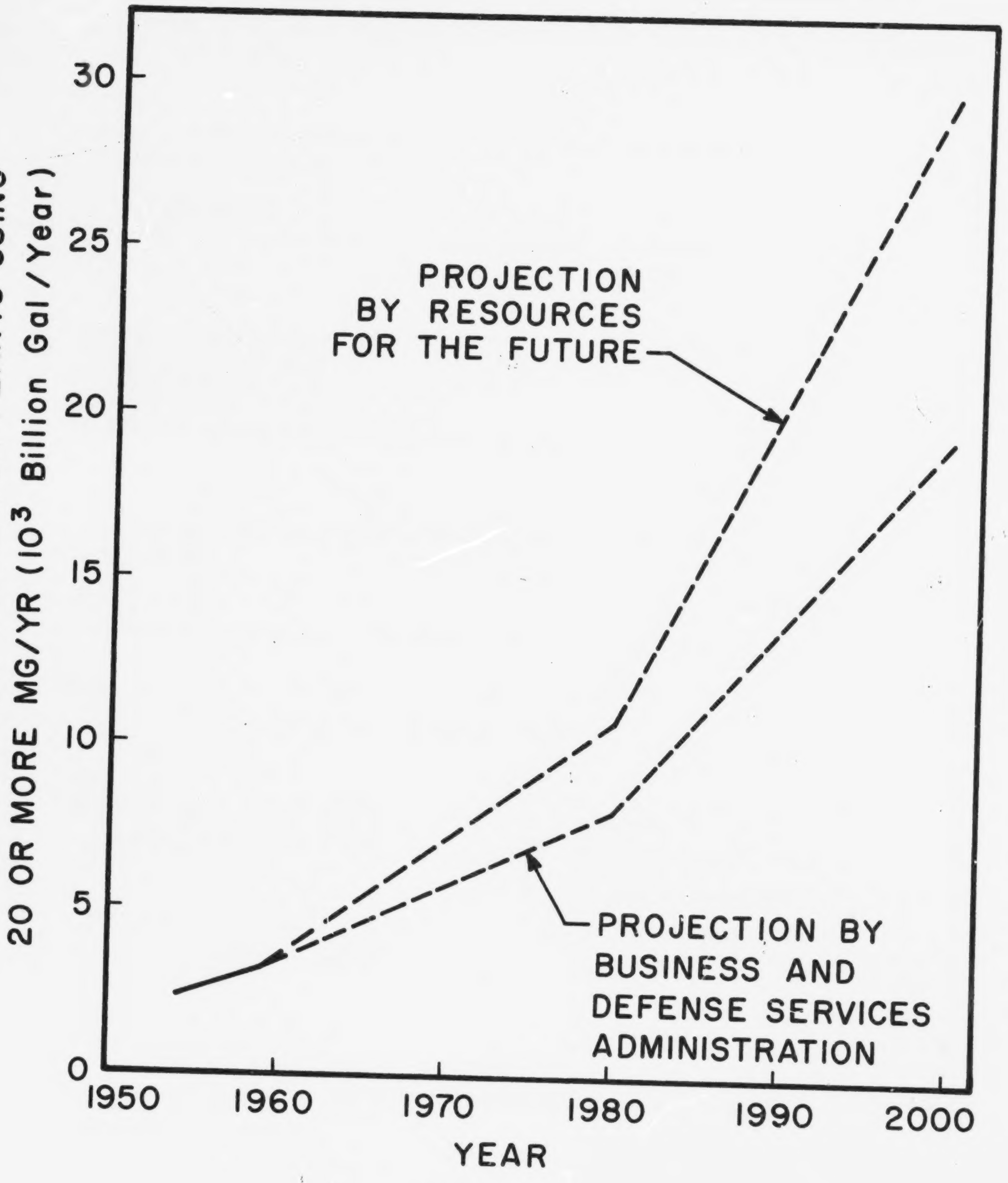


FIGURE I-4

TOTAL WATER INTAKE FOR CHEMICAL AND ALLIED PRODUCTS INDUSTRY

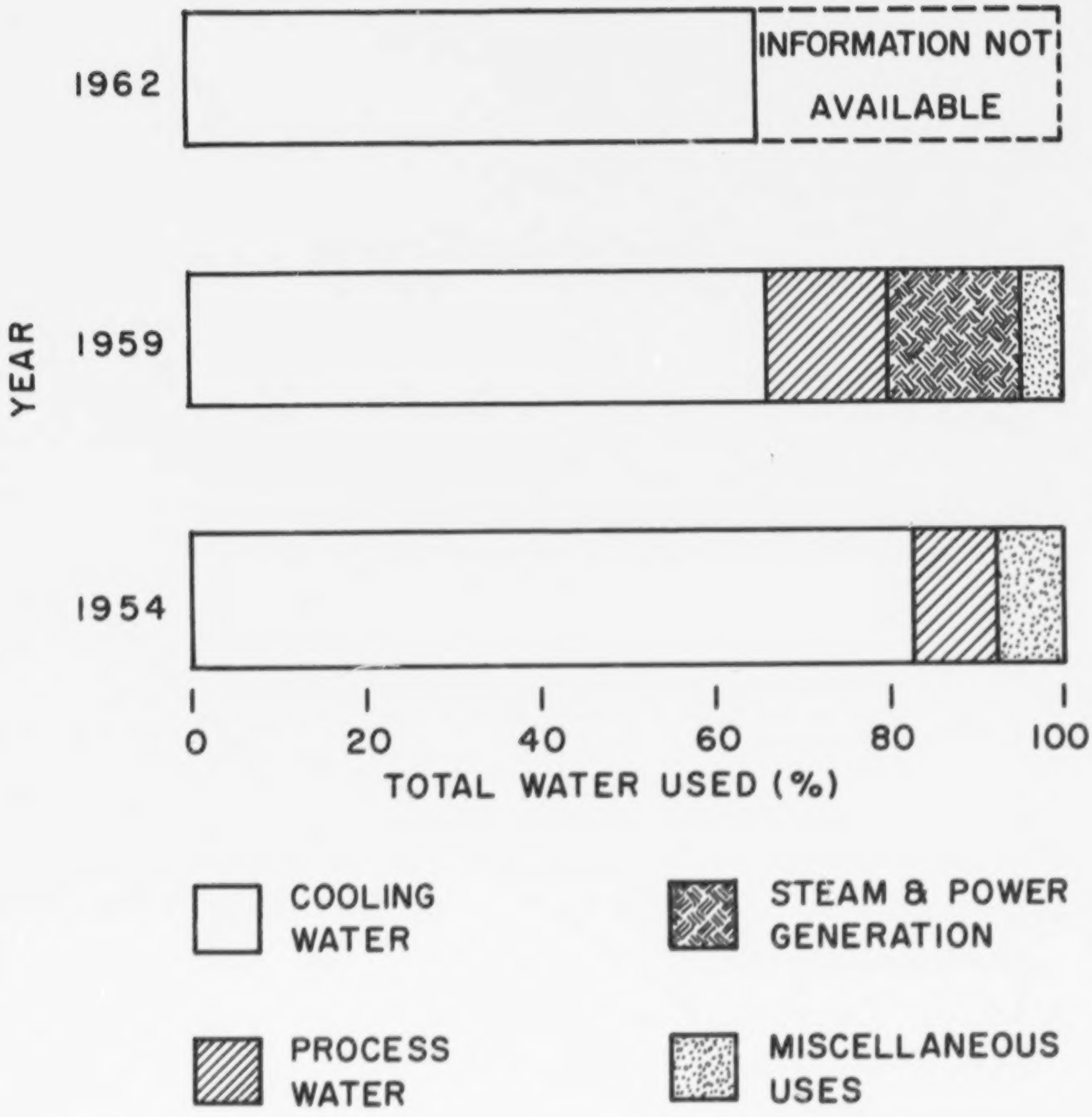


FIGURE I-5

CLASSIFICATION OF WATER USED BY THE PETROCHEMICAL INDUSTRY

REFERENCES - CHAPTER I

1. Aalund, L., "Petrochemical Activity Hits a New High Around the World," The Oil and Gas Journal, v. 65, p. 108 (Sept. 4, 1967).

2. Anon., 1954 Census of Manufacturers: Industrial Water Use Supplement, U. S. Dept. of Commerce, Bureau of the Census, Bull. MC-209 Supp., Washington, D. C. (1957).

3. Anon., 1958 Census of Manufacturers, Summary of Statistics, v. 1, U. S. Dept. of Commerce, Bureau of the Census, Washington, D. C. (1961).

4. Anon., The Petroleum Handbook, Shell International Petroleum Co., Ltd., 5th Edition, Balding and Mansell, Ltd. eds., London (1966).

5. Anon., Water in Industry, National Assoc. of Manufacturers and The Conservation Foundation, New York, N. Y. (1950).

6. Anon., Water in Industry, National Assoc. of Manufacturers and Chamber of Commerce of the United States, New York and Washington, D. C. (1965).

7. Anon., "Why Petrochemicals Are Appealing," Business Week, Special Rept. p. 56 (Sept. 3, 1960).

8. Goldstein, R. F., The Petroleum Chemicals Industry, 2nd Edition, Spon, London (1958).

9. Lewis, N. J., "Natural Gas Liquids For Petrochemicals: How Big?" Hydrocarbon Processing, v. 45, n. 6, p. 195 (June 1966).

10. Sawyer, F. G., "Best Picks for '66: Petrochemicals," Hydrocarbon Processing, v. 45, n. 1, p. 161 (Jan. 1966).

11. Senate Reports, Future Water Requirements of Principal Water-Using Industries, Select Committee on National Water Resources, 86th Congress Committee Print No. 8 (1960).

12. Stanley, H. M., The Petroleum-Chemicals Industry, Lecture Series 1963, No. 4, The Royal Institute of Chemistry (1963).

BLANK PAGE

CHAPTER II

DESCRIPTION OF THE PETROCHEMICAL INDUSTRY

"Petrochemicals" can be defined as any chemicals which are derived from petroleum or natural gas. The phrase "petroleum-chemicals" is preferred by some authors who dislike the former expression; but, in general, the term "petrochemical" is acceptable.

The variety of chemicals that are petroleum-based is enormous, and it would be impossible to prepare a complete list of petrochemical products. Profiles of major petrochemical products, however, are presented in Appendix I.

Many of the petrochemicals as defined herein are difficult to categorize according to the Standard Industrial Classification (SIC) numbers, although the applicable categories based on 1967 revisions include: SIC 2813 (industrial gases), SIC 2815 (cyclic intermediates, dyes, organic pigments, and crudes), SIC 2818 (organic chemicals), SIC 2819 (inorganic chemicals derived from petroleum), SIC 2821 (plastic materials and resins), SIC 2871 (agricultural fertilizers), and SIC 2873 (insecticides).

Petroleum-chemicals can be divided into two principal categories, organics and inorganics. One exception to this division is carbon black, a complex chemical which can be classified neither completely organic nor completely inorganic but still is considered a petrochemical since petroleum is its principal source (Sherwood, 1964). In 1953, approximately 70 percent of the carbon black produced was used as a reinforcing agent in rubber for tires (Conklin, 1953).

The furnace process and the contact process are used for the production of carbon black. Both processes produce an extremely fine powder which is normally pelletized using a small amount of water to render the carbon black amenable to packaging and shipping. The furnace method requires additional water for cooling the furnace gases and for capture of entrained carbon black. The hydrocarbon feedstocks used to produce carbon black are varied, ranging from crude petroleum to pure methane.

PRINCIPAL PETROCHEMICAL PRODUCTS AND INTERMEDIATES

In order to better illustrate the processing of petroleum chemicals from raw material to final product, schematic diagrams have been prepared. The primary or first-generation petrochemicals derived directly from the petroleum raw materials are shown in Figure II-1. With the exception of carbon black, which is not further

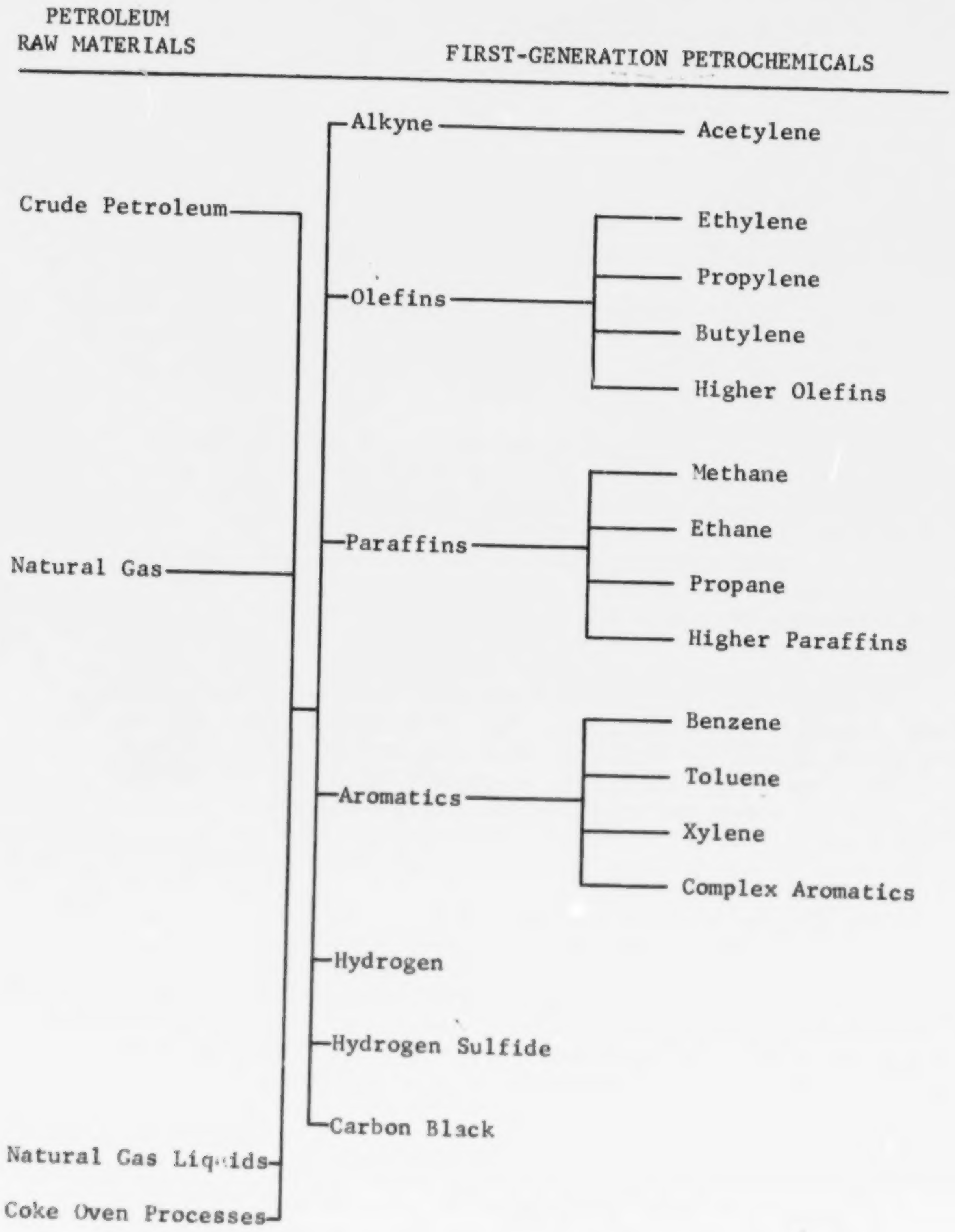

PETROLEUM RAW MATERIALS
FIRST-GENERATION PETROCHEMICALS
Crude Petroleum
Natural Gas
Natural Gas Liquids
Coke Oven Processes
Alkyne
Acetylene
Olefins
Ethylene
Propylene
Butylene
Higher Olefins
Paraffins
Methane
Ethane
Propane
Higher Paraffins
Aromatics
Benzene
Toluene
Xylene
Complex Aromatics
Hydrogen
Hydrogen Sulfide
Carbon Black

FIGURE II-1

FIRST GENERATION PETROCHEMICALS

processed, all petrochemical products come from these primary chemicals. The processes used in the conversion of raw petroleum to these first-generation chemicals will be subsequently described. These primary petrochemicals are followed through their intermediate products to their end-products by Figures II-2 through II-5. Actually, most of the products shown in these figures are not the final products used by the consumer, but instead represent the raw materials used by the industries in preparing consumer goods. The final stages of manufacturing are not included in this report because they ordinarily are considered to be outside the realm of the "petrochemical" industry.

Categorization of Products

Each of the groups of first-generation petrochemicals is considered separately. For example, the principal products manufactured from the olefins are illustrated in Figure II-2. The products obtained ~~by~~ using olefins as the chemical base are divided into six categories: bases for plastics and resins, synthetic rubber bases, synthetic fiber bases, components of synthetic detergents, basic industrial chemicals, and basic chemicals for agriculture. Obviously, many more subdivisions would be possible, but to prevent an excessively complicated categorization, these six were chosen and are appropriate for an investigation of this scope.

The category of basic industrial chemicals includes the miscellaneous olefin products. These chemicals have a broad application in industry in solvents; paint, varnish, and other surface coating ingredients; pharmaceuticals, food processing and automotive chemicals; and a myriad of other products which could not be placed in one of the other five categories.

This system of product classification was used for each of the primary petrochemical groupings shown in Figure II-1. Inorganics and some miscellaneous hydrocarbons are classified together in Figure II-5. Carbon black, which can be obtained directly from raw petroleum or from primary petrochemicals, also is included under the primary petrochemicals from which it is formed.

There are several families of organic compounds which contain only carbon and hydrogen in their molecules. These compounds are termed "hydrocarbons" and almost every petrochemical product which is organic based, and most of them are, is based on a hydrocarbon raw material. The principal hydrocarbons used by the petrochemical industry include the olefins, the aromatics, and the paraffins. These families of compounds constitute the primary petrochemicals and must be separated from the raw petroleum before they can be used as feedstocks for chemical processes. A brief discussion of each of these primary groups of compounds will indicate how they are obtained and used.

Olefins - Olefins, principally ethylene and propylene, are the commercial bases for the majority of synthetic organic chemicals produced in the United States (Stephenson, 1966). The olefins, also

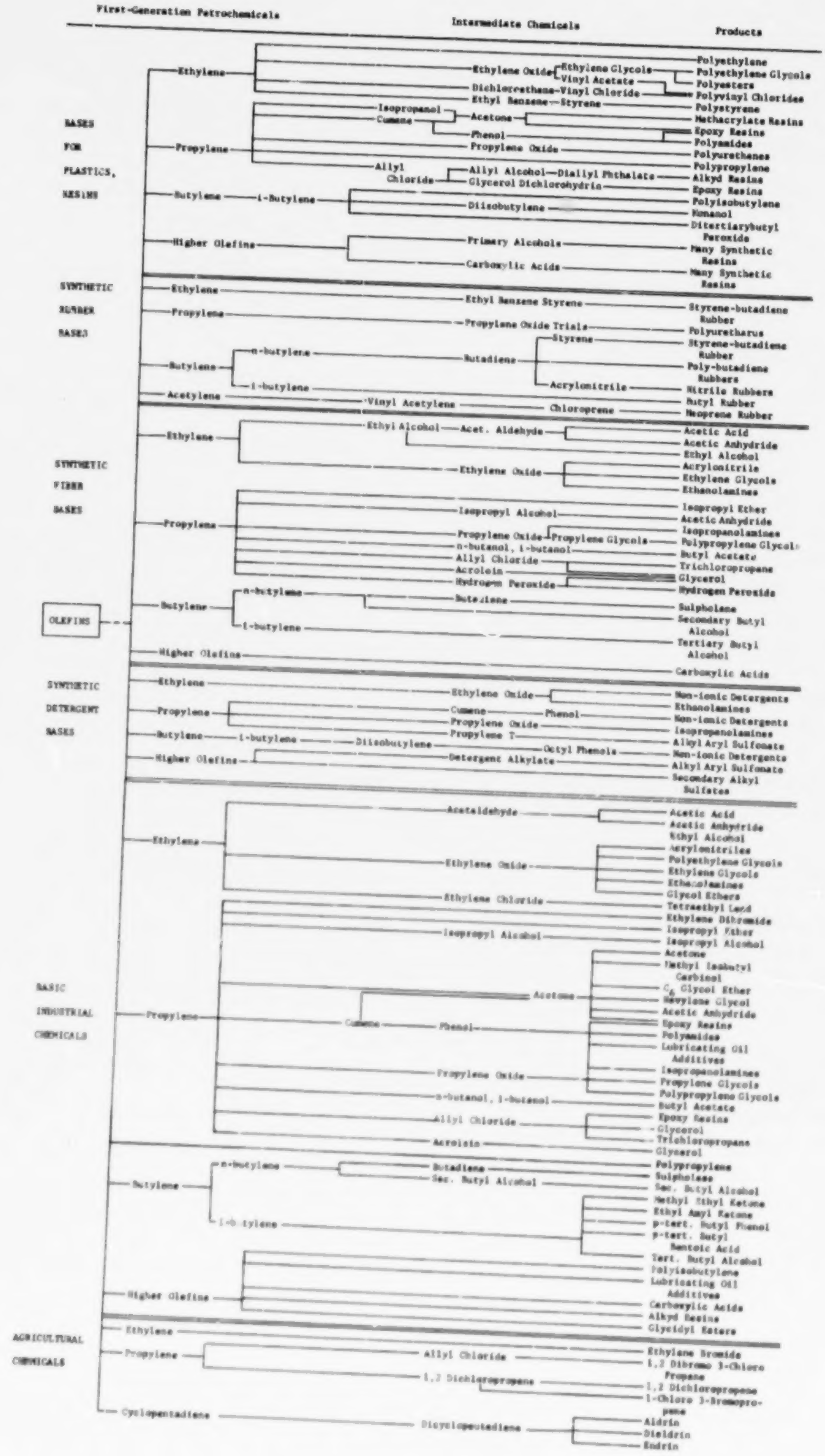

First-Generation Petrochemicals
Intermediate Chemicals
Products
BASES FOR PLASTICS, RESINS
Ethylene
Polyethylene
Ethylene Oxide
Ethylene Glycols
Polyethylene Glycols
Vinyl Acetate
Polyesters
Dichlorethane-Vinyl Chloride
Polyvinyl Chlorides
Ethyl Benzene—Styrene
Polystyrene
Propylene
Isopropanol
Cumene
Acetone
Methacrylate Resins
Phenol
Epoxy Resins
Polyamides
Propylene Oxide
Polyurethanes
Polypropylene
Allyl Chloride
Allyl Alcohol—Diallyl Phthalate
Alkyd Resins
Glycerol Dichlorohydrin
Epoxy Resins
Butylene
i-Butylene
Polyisobutylene
Diisobutylene
Nonanol
Ditertiarybutyl Peroxide
Higher Olefins
Primary Alcohols
Many Synthetic Resins
Carboxylic Acids
Many Synthetic Resins
SYNTHETIC RUBBER BASES
Ethylene
Ethyl Benzene Styrene
Styrene-butadiene Rubber
Propylene
Propylene Oxide Trials
Polyuretharus
Butylene
n-butylene
Butadiene
Styrene
Styrene-butadiene Rubber
Poly-butadiene Rubbers
i-butylene
Acrylonitrile
Nitrile Rubbers
Acetylene
Butyl Rubber
Vinyl Acetylene
Chloroprene
Neoprene Rubber
SYNTHETIC FIBER BASES
Ethylene
Ethyl Alcohol
Acet. Aldehyde
Acetic Acid
Acetic Anhydride
Ethyl Alcohol
Ethylene Oxide
Acrylonitrile
Ethylene Glycols
Ethanolamines
Propylene
Isopropyl Alcohol
Isopropyl Ether
Acetic Anhydride
Propylene Oxide
Propylene Glycols
Isopropanolamines
Polypropylene Glycols
n-butanol, i-butanol
Butyl Acetate
Allyl Chloride
Trichloropropane
Acrolein
Glycerol
Hydrogen Peroxide
Hydrogen Peroxide
OLEFINS
Butylene
n-butylene
Butadiene
Sulpholene
Secondary Butyl Alcohol
i-butylene
Tertiary Butyl Alcohol
Higher Olefins
Carboxylic Acids
SYNTHETIC DETERGENT BASES
Ethylene
Ethylene Oxide
Non-ionic Detergents
Ethanolamines
Propylene
Cumene
Phenol
Non-ionic Detergents
Propylene Oxide
Isopropanolamines
Butylene
i-butylene
Diisobutylene
Propylene T
Alkyl Aryl Sulfonate
Octyl Phenols
Non-ionic Detergents
Higher Olefins
Detergent Alkylate
Alkyl Aryl Sulfonate
Secondary Alkyl Sulfates
BASIC INDUSTRIAL CHEMICALS
Ethylene
Acetaldehyde
Acetic Acid
Acetic Anhydride
Ethyl Alcohol
Ethylene Oxide
Acrylonitriles
Polyethylene Glycols
Ethylene Glycols
Ethanolamines
Glycol Ethers
Ethylene Chloride
Tetraethyl Lead
Ethylene Dibromide
Propylene
Isopropyl Alcohol
Isopropyl Ether
Isopropyl Alcohol
Acetone
Acetone
Methyl Isobutyl Carbinol
C_6 Glycol Ether
Hexylene Glycol
Acetic Anhydride
Cumene
Phenol
Epoxy Resins
Polyamides
Lubricating Oil Additives
Propylene Oxide
Isopropanolamines
Propylene Glycols
Polypropylene Glycols
n-butanol, i-butanol
Butyl Acetate
Allyl Chloride
Epoxy Resins
Glycerol
Trichloropropane
Acrolein
Glycerol
Butylene
n-butylene
Butadiene
Polypropylene
Sulpholene
Sec. Butyl Alcohol
Sec. Butyl Alcohol
i-butylene
Methyl Ethyl Ketone
Ethyl Amyl Ketone
p-tert. Butyl Phenol
p-tert. Butyl Benzoic Acid
Tert. Butyl Alcohol
Higher Olefins
Polyisobutylene
Lubricating Oil Additives
Carboxylic Acids
Alkyd Resins
Glycidyl Esters
AGRICULTURAL CHEMICALS
Ethylene
Ethylene Bromide
Propylene
Allyl Chloride
1,2 Dibromo 3-Chloro Propane
1,2 Dichloropropene
1,2 Dichloropropene
1-Chloro 3-Bromopropene
Cyclopentadiene
Dicyclopentadiene
Aldrin
Dieldrin
Endrin

FIGURE II-2

PRINCIPAL PRODUCT DERIVATIVES FROM THE OLEFINS

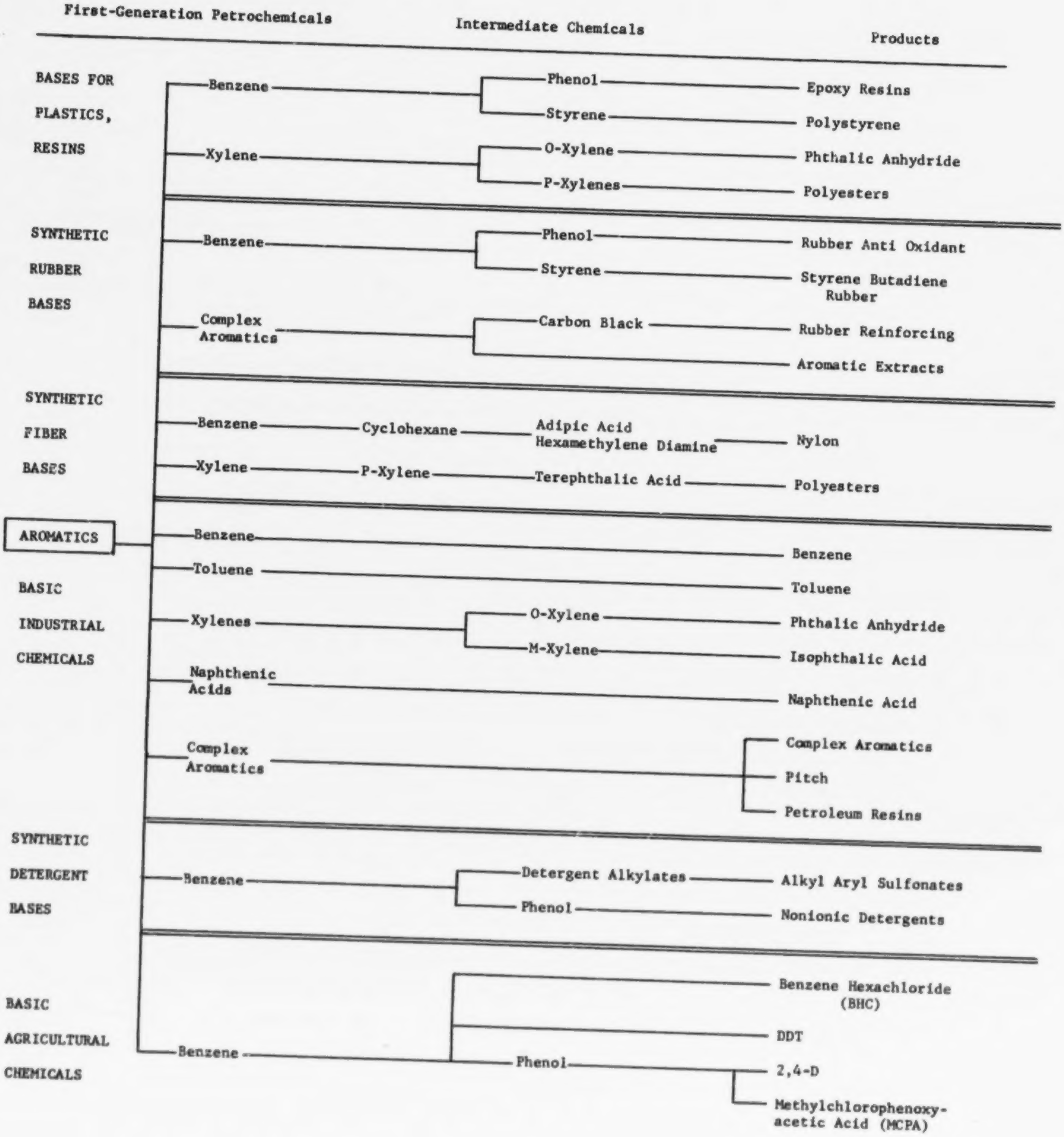

First-Generation Petrochemicals
Intermediate Chemicals
Products
BASES FOR PLASTICS, RESINS
Benzene
Phenol
Epoxy Resins
Styrene
Polystyrene
Xylene
O-Xylene
Phthalic Anhydride
P-Xylenes
Polyesters
SYNTHETIC RUBBER BASES
Benzene
Phenol
Rubber Anti Oxidant
Styrene
Styrene Butadiene Rubber
Complex Aromatics
Carbon Black
Rubber Reinforcing
Aromatic Extracts
SYNTHETIC FIBER BASES
Benzene
Cyclohexane
Adipic Acid
Hexamethylene Diamine
Nylon
Xylene
P-Xylene
Terephthalic Acid
Polyesters
AROMATICS
Benzene
Benzene
Toluene
Toluene
BASIC INDUSTRIAL CHEMICALS
Xylenes
O-Xylene
Phthalic Anhydride
M-Xylene
Isophthalic Acid
Naphthenic Acids
Naphthenic Acid
Complex Aromatics
Complex Aromatics
Pitch
Petroleum Resins
SYNTHETIC DETERGENT BASES
Benzene
Detergent Alkylates
Alkyl Aryl Sulfonates
Phenol
Nonionic Detergents
BASIC AGRICULTURAL CHEMICALS
Benzene
Benzene Hexachloride (BHC)
DDT
Phenol
2,4-D
Methylchlorophenoxy-acetic Acid (MCPA)

FIGURE II-3

PRINCIPAL PRODUCT DERIVATIVES FROM THE AROMATICS

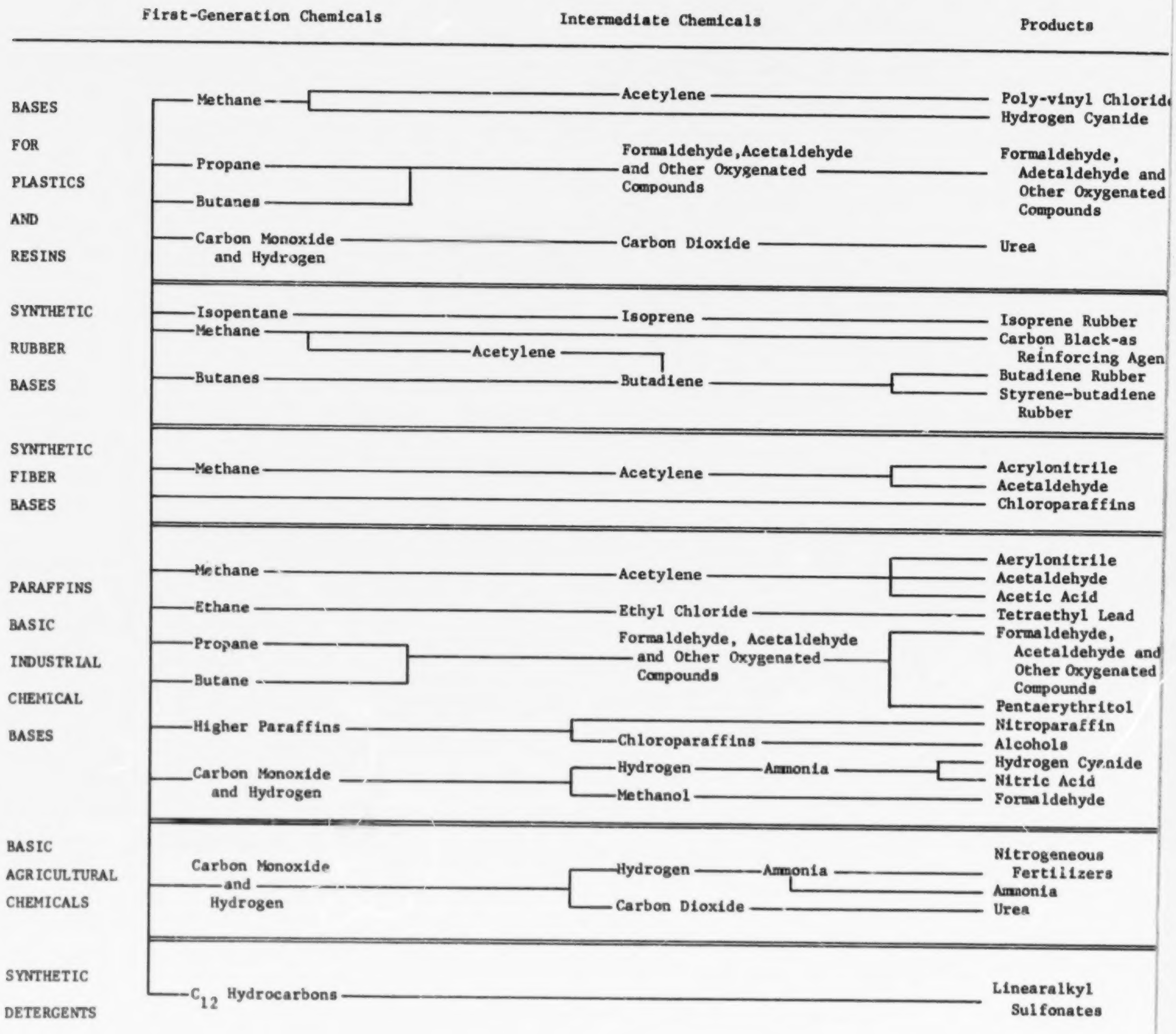

First-Generation Chemicals
Intermediate Chemicals
Products
BASES FOR PLASTICS AND RESINS
Methane
Acetylene
Poly-vinyl Chlorid
Hydrogen Cyanide
Propane
Butanes
Formaldehyde,Acetaldehyde and Other Oxygenated Compounds
Formaldehyde, Adetaldehyde and Other Oxygenated Compounds
Carbon Monoxide and Hydrogen
Carbon Dioxide
Urea
SYNTHETIC RUBBER BASES
Isopentane
Isoprene
Isoprene Rubber
Methane
Carbon Black-as Reinforcing Agen
Acetylene
Butanes
Butadiene
Butadiene Rubber
Styrene-butadiene Rubber
SYNTHETIC FIBER BASES
Methane
Acetylene
Acrylonitrile
Acetaldehyde
Chloroparaffins
PARAFFINS BASIC INDUSTRIAL CHEMICAL BASES
Methane
Acetylene
Aerylonitrile
Acetaldehyde
Acetic Acid
Ethane
Ethyl Chloride
Tetraethyl Lead
Propane
Butane
Formaldehyde, Acetaldehyde and Other Oxygenated Compounds
Formaldehyde, Acetaldehyde and Other Oxygenated Compounds
Pentaerythritol
Higher Paraffins
Chloroparaffins
Nitroparaffin
Alcohols
Carbon Monoxide and Hydrogen
Hydrogen
Ammonia
Hydrogen Cyanide
Nitric Acid
Methanol
Formaldehyde
BASIC AGRICULTURAL CHEMICALS
Carbon Monoxide and Hydrogen
Hydrogen
Ammonia
Nitrogeneous Fertilizers
Ammonia
Carbon Dioxide
Urea
SYNTHETIC DETERGENTS
C_{12} Hydrocarbons
Linearalkyl Sulfonates

FIGURE II-4

PRINCIPAL PRODUCT DERIVATIVES FROM THE PARAFFINS

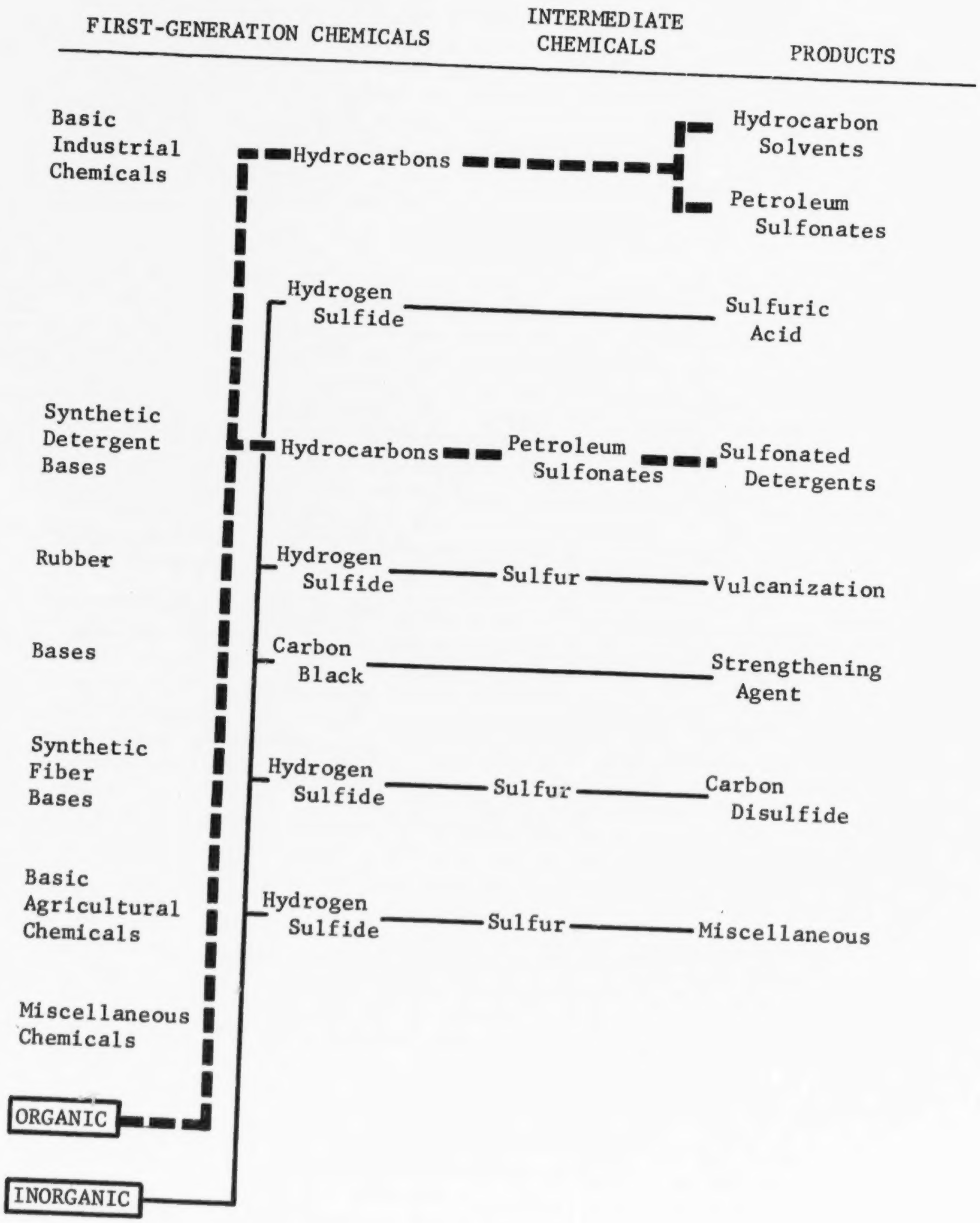

FIRST-GENERATION CHEMICALS
INTERMEDIATE CHEMICALS
PRODUCTS
Basic Industrial Chemicals
Hydrocarbons
Hydrocarbon Solvents
Petroleum Sulfonates
Hydrogen Sulfide
Sulfuric Acid
Synthetic Detergent Bases
Hydrocarbons
Petroleum Sulfonates
Sulfonated Detergents
Rubber
Hydrogen Sulfide
Sulfur
Vulcanization
Bases
Carbon Black
Strengthening Agent
Synthetic Fiber Bases
Hydrogen Sulfide
Sulfur
Carbon Disulfide
Basic Agricultural Chemicals
Hydrogen Sulfide
Sulfur
Miscellaneous
Miscellaneous Chemicals
ORGANIC
INORGANIC

FIGURE II-5

PRINCIPAL PRODUCT DERIVATIVES FROM MISCELLANEOUS SOURCES known as alkenes, are characterized by a highly reactive double bond which renders them extremely useful in a variety of synthesis reactions. Each double bond in a compound indicates that two fewer hydrogen atoms will be present than the maximum which can exist in a hydrocarbon. This is termed "unsaturation." Dienes, which contain two double bonds, are not strictly olefins by definition but undergo similar reactions. The most important diene, and one of the more important petrochemicals, is 1,3 butadiene, a major component of many synthetic rubbers (Noller, 1958).

Some of the main chemical processes for the conversion of olefins into chemical derivatives are polymerization, hydration, halogenation, epoxidation, alkylation, and hydrocarboxylation (Stanley, 1963). The most important products which originate from olefins are illustrated in Figure II-2. Ethylene is by far the most important petrochemical raw material. The distribution of the principal uses for ethylene are given in Table II-1. Propylene, although not produced in the same quantities as ethylene, is also an extremely important petrochemical feedstock, and the chemical products derived from it are listed in Table II-1. With the exception of the butylene used in the manufacture of butadiene, the four-carbon and higher olefins are not widely used in chemical manufacture.

Aromatics - All aromatic compounds can be considered derivatives of benzene, and thus a discussion of the characteristics and reactions of benzene will apply to the rest of the aromatics. The molecular formula of benzene is C_6H_6 which would seem to indicate that this compound, like the olefins, would be highly unsaturated; however, the aromatic ring has been found to be almost as stable as completely saturated hydrocarbons. This stability indicates that double bonds found in the olefins are not present in benzene or the other aromatics. It is now believed that the six carbon atoms in the benzene molecule are arranged in a ring, connected to each other by a hybrid bond having properties intermediate between those of a single bond and a double bond (Noller, 1958). These hybrid bonds are all of equal strength and are relatively unreactive. However, the hydrogen atoms of the aromatic nucleus are more readily substituted than those on saturated hydrocarbons. The principal petrochemical reactions of aromatics involve substitution of these hydrogens and include halogenation, nitration, sulfonation, oxidation of side-chains, alkylation, and the Friedel-Crafts reaction which results in ketone formation when an aromatic is reacted with an acyl halide.

The aromatics rank second only to the olefins in terms of quantities of primary organic petrochemicals produced annually. Substantial amounts of these aromatics are still produced from coal and coke, but petroleum-based aromatics are satisfying the increased demand for these chemicals. Benzene is the most important of the aromatics in terms of quantity produced, and in 1964, approximately 84 percent of the total benzene production came from petroleum-based raw materials (Sawyer, 1966). With the exception of naphthalene, all of the common aromatic chemicals are derived principally from petroleum hydrocarbons.

TABLE II-1

PERCENTAGE OF ETHYLENE AND PROPYLENE REQUIRED FOR VARIOUS PRODUCTS

(Reference 20)

Product	% Total Ethylene Used For Particular Product
Polyethylene	30
Ethylene Oxide	24
Ethanol	17
Ethylbenzene	8
Ethylene Dichloride	7
Other	14

Product	% Total Propylene Used For Particular Product
Isopropanol	37
Propylene Trimer, Tetramer	23
Polypropylene	13
Propylene Oxide	12
Cumene	6.5
Other	8.5

Some of the chemical products and intermediates which are manufactured from aromatics are illustrated in Figure II-3. Obviously, the schematic is not complete, but it does give a representation of the major aromatic-derived chemical products.

Paraffins - Paraffins, also known as alkanes, are the simplest family of hydrocarbons. All members of the aliphatic or acyclic series (straight-chain compounds) can be considered to be derived from them (Noller, 1958). The simplest constituent of this class of compounds is methane, CH_4. All other members of this family differ from methane by multiples of one carbon and two hydrogen atoms, that is, by CH_2. All of the paraffins with four carbon atoms or less are gases at standard temperature and pressure, while those with five or more carbons are liquids or solids. Paraffins with four or more carbon atoms can exist in branched forms, the number of possible isomers of each compound increasing with the number of carbons.

Paraffins are the least reactive of the hydrocarbons and all of the common processing steps require elevated temperatures and pressures. The most important paraffin reactions include dehydrogenation and cracking, which produce olefins, the principal petrochemical feedstocks. Chlorination and isomerization are also utilized to a lesser extent by the petrochemical industry.

Naphthenes, of which cyclopentane and cyclohexane are the most important in the petrochemical industry, can be considered special types of paraffins. These compounds have a ring structure, but unlike aromatic compounds, the carbon-carbon bonds exhibit exactly the same characteristics as the bonds in the paraffins.

The principal paraffinic feedstocks used by the chemical industry are the one- to five-carbon hydrocarbons (Sherwood, 1964). Straight-chain paraffins in the twelve-carbon range are now becoming important in the manufacture of the new biodegradable detergents (Sherwood, 1964). Large quantities of ethane and propane are converted to ethylene since the demand for this petrochemical far exceeds its availability. Other manufactured products using paraffins as the base-chemical such as synthesis gas, a mixture of carbon monoxide and hydrogen, are shown in Figure II-4.

Miscellaneous Petrochemicals - Other petrochemicals not categorized in the strictest sense in the previous headings are also important. Hydrocarbon solvents, such as white gas, containing both paraffins and aromatics are manufactured in the normal course of refining operations (Anon., Shell, 1966). These solvents are classified according to their aromatic content.

Sulfur is also an important petrochemical which is obtained primarily in the form of hydrogen sulfide during the refining of crude oil. The principal uses for the miscellaneous petrochemicals are shown in Figure II-5.

PROJECTED GROWTH OF THE PETROCHEMICAL INDUSTRY

The petrochemical industry has grown tremendously during the past two decades. In the eight-year period from 1955 to 1963, production of organic petrochemicals more than doubled (Sherwood, 1963). Estimates of projected production capacity of particular petrochemicals or products are constantly revised to reflect changes in processes, consumer demands, and feedstocks. The projected data in Table II-2 presents current estimates of consumption in 1975 for the more important petrochemicals and products. Some of these estimates were made as early as 1955, however, and the accuracy of these projections is subject to question.

Several factors have been important in the rapid development of the petrochemical industry. These factors include the use of petroleum rather than alternative sources as a raw material, the expansion of markets for petrochemical products, and the development of new commercial petrochemical products. Future demand for petrochemicals and their products will be controlled by developments in the end-use markets and newly developed products (Sherwood, 1963). Petroleum has already essentially displaced alternate raw materials in the manufacture of products having multiple raw material sources.

The outlook for growth in the entire petrochemical industry is favorable. In 1955, petrochemical production constituted about 24 percent by weight of total chemical production; by 1970, it should account for 41 percent according to this projection (McGrath, 1961). However, the rapid growth of the industry may prove this estimate to be conservative. On the basis of sales, the growth of this industry is equally impressive. Petrochemical sales for 1966 were estimated to be $12 billion and projected sales for 1970 exceed $20 billion (Anon., Bus. Wk.,1966). The 1966 projection of petrochemical sales for 1970 was about $5 billion higher than a similar projection made in 1961. Petrochemicals should account for 64 percent of the total dollar value of all chemical products.

Growth of the petrochemical industry is also reflected by the number of projects planned or under construction. In 1967, 81 new petrochemical projects were in the planning or construction stage in the United States, compared to 41 the previous year (Aalund, 1967). Global capital outlay for new petrochemical facilities was $2.4 billion in 1965 (Sawyer, 1966).

In order to continually grow and expand, the petroleum industry must be assured of sufficient quantities of raw materials. If raw materials continue to be used at the consumption rates reported in 1967, the nation's proven reserves of crude oil and natural gas liquids will be consumed in nine years, and the natural gas reserves will be exhausted in sixteen years (Anon., Chem. & Engr. News., April 15, 1968). It is interesting to note that while

TABLE II-2

PROJECTION OF UNITED STATES PETROCHEMICAL PRODUCTION CAPACITY FOR SELECTED CHEMICALS

(References 1, 5, 21)

Products and Petrochemical Intermediates	United States Production - billions of pounds/year		
	1954	Recent Data year in parentheses	1975+
Synthetic Fibers			
Acetate	0.34		1.12
Acetic Anhydride	0.696*		2.65*
Nylon	-		0.8-1.0
Polyesters	0.035		1.0
Acrylic Fibers	0.097		1.5-1.6
Acrylonitrile	0.2*		1.5*
Plastics and Resins	2.8	7.74 (1962)	
Phenolic Resins	0.434	0.66 (1962)	1.6*
Phenol	0.6*		2.25*
Formaldehyde	1.03*		7.25*
Phthalic Alkyd and Nonbenzenoid Alkyd Resins	0.45	0.53 (1962)	1.66
Phthalic Anhydride	-		-
Synthetic Glycerol	0.115*		0.915*
Styrene Resins	0.481	1.25 (1962)	2.4
Styrene	0.500		2.4
Urea and Melamine Resins	0.265		0.715
Vinyl Resins	0.524	1.55 (1962)	2.5
Polyolefins	-	2.16 (1962)	-
Polyethylene	0.57	4 (1967)	6.93
Polypropylene		0.66 (1967)	2.11
Surface-Active Agents (Not Detergents Themselves)	1.03		1.6
Ethanolamines	0.063		0.153

TABLE II-2 (Continued)

PROJECTION OF UNITED STATES PETROCHEMICAL PRODUCTION CAPACITY FOR SELECTED CHEMICALS

Products and Petrochemical Intermediates	United States Production - billions of pounds/year		
	1954	Recent Data year in parentheses	1975+
Synthetic Rubber	1.31		5.6
Copolymer	0.97		4.35
Butyl	0.13		0.4
Neoprene	0.16		0.58
Others	0.052		0.27
Ammonia (from petroleum only)	6.8		11.2
Methanol	1.1		3.6
Methyl Chloride	0.04		0.15
Ethyl Chloride	0.4		1.46
Ethylene Dichloride	0.53		2.1
Ethanol (Synthetic)	1.44		4.9
Ethylene Glycol	0.97		1.6
Ethylene Oxide		15.1 (1967)	21.0
Ethylene			17.3(1971)

+ Estimated Consumption

* Includes Other Uses for Intermediate

thousands of different petrochemicals are manufactured, fewer than 100 chemically different products constitute over 90 percent of the total sales of organic chemical intermediates (Sherwood, 1963). The following discussion will briefly elaborate on the prospective growth for the more important petrochemicals and products.

Plastics and Resins

Plastics and resins, which are primarily used as construction and packaging materials, are the most important petrochemical products in terms of volume and projected growth (Stockton, et. al., 1959). In 1962, 7.7 billion pounds of these materials were produced in the United States with a corresponding domestic consumption of over 6.9 billion pounds (Sherwood, 1963).

Polyolefins constitute the most important petrochemical category in the plastic industry. By 1975, the world demand for polyolefins should approach 35.2 billion pounds, four times greater than the 1965 global output of these materials (Anon., Oil & Gas J., 1966). United States polyethylene production is expected to increase 160 percent by 1975 (Anon., Bus. Wk., 1966). The importance of polypropylene is also coming into focus. The production of this propylene derivative has risen from 643 million pounds in 1967 to an expected 825 million pounds in 1968. The 1969 production of polypropylene is predicted to be one billion pounds. (Anon., Chem. & Engr. News., August 5, 1968). The polypropylene plastics should account for 7.5 percent of the world polyolefin market by 1975 (Anon., Oil & Gas J., 1966). There are indications that a 350 percent increase can be expected in polypropylene production from 1966 to 1975 (Anon., Bus. Wk., 1966); however, the production of propylene could influence the availability of polypropylene and other propylene derivatives. Consumption of propylene is expected to exceed seven billion pounds in 1968 and this should continue to increase 10 percent annually for the next five years. Producers of propylene-based products, such as polypropylene and acrylonitrile, are concerned that limited supplies of propylene will restrict future output of these derivatives (Anon., Chem. & Engr. News., August 5, 1968).

Projections for 1970 indicate that propylene demand for chemical use will exceed supply and the price will increase from 2.2¢/lbs to 2.5¢/lb. There appears to be a need to manufacture propylene by a direct process, since propylene is presently produced only as a by-product of ethylene manufacture. Propylene availability is therefore a function of ethylene demand. Because of the low unit price of propylene, it is not expected that presently available processes, such as pyrolysis, catalytic dehydrogenation, or oxidative dehydrogenation (using I_2) of propane will be economically justified in the next decade (Anon., Hydroc. Proc., April 1968).

The production and consumption of other plastics and resins are also expanding. United States consumption of vinyl compounds increased by 20 percent in 1962 while current annual growth of the styrene resins is about 12 percent (Sherwood, 1963). Production of propylene oxide could top 880 million pounds in 1968, a 1[illegible] percent gain over 1967. The strong demand is based on two major products from propylene oxide, urethane foam and unsaturated polyesters (Anon., Chem. & Engr. News.,July 8, 1968). Other plastics and resins are currently growing at annual rates of two to four percent.

Synthetic Fibers

Synthetic fibers constitute an important part of the total petrochemical output. World nylon consumption is expected to increase from two billion pounds in 1964 to 3.3 billion pounds in 1975 (Sherwood, 1966). It is estimated that the United States will provide about 40 percent of the world nylon production capacity. Polyester resins, used in textiles and tire cords, should double in production capacity between 1966 and 1975, while the production of acrylonitrile, used in the manufacture of acrylic fibers such as dacron, should increase 165 percent during the same time period (Anon., Bus. Wk.,1966). Polypropylene fiber producers are about to contest for many of the textile markets now held by the big three synthetic fibers: namely, nylon, polyester, and acrylic (Anon., Chem. & Engr. News.,May 27, 1968).

Synthetic Rubber

In 1966, synthetic rubber accounted for 75 percent of total rubber produced, and this fraction should increase to 82 percent by 1975 (Sawyer, 1966). About 63 percent of the United States' synthetic rubber production is used in tires and related products (Sherwood, 1963). The average annual rate of increase of synthetic rubber consumption is expected to be about four percent. Styrene-butadiene rubber constituted 77.4 percent of United States production in 1963, but this figure is expected to be reduced to approximately 59 percent by 1970 (Sherwood, 1963; Anon., Oil & Gas J.,,1966). New types of synthetic rubbers are rapidly becoming important in the general purpose rubber market. The demand for the stereo-specific rubbers, such as cis-polybutadiene and cis-polyisoprene is expected to triple in the next five years when they are expected to occupy 14 percent of the total synthetic rubber market (Anon., Oil & Gas J.,1966). Production of ethylene-propylene rubbers should increase by 90 percent between 1966 and 1975 (Anon., Bus. Wk.,1966).

Other Petrochemical Products and Intermediates

The data in Table II-2 also list selected important petrochemical products and intermediates which are not included in the major categories previously discussed. Petrochemicals are the primary raw materials used in the manufacture of synthetic detergents, pesticides, solvents, automotive chemicals, and a myriad of other minor products.

Two additional important chemicals should be mentioned. Ammonia is one of the most important petrochemicals in terms of production capacity. By 1970 the global production capacity of nitrogen should reach 50.3 million tons/year, compared with a 1965 capacity of 26.5 million tons/year (Aalund, 1967). In 1967, the United State's capacity for ammonia production was 17.3 million tons/year, an increase of 33 percent over the previous year. Another three million tons/year of ammonia production capacity is scheduled for operation by 1969.

The production of ethylene, the most important petrochemical intermediate, has also grown rapidly. Currently annual consumption of ethylene is about 14 million metric tons, and it is predicted that the demand will rise by more than 25 million metric tons between 1970 and 1980. The petrochemical industry probably will add 10 to 15 new ethylene plants each year (Anon., Chem. & Engr. News., October 14, 1968). A firm in Houston, Texas predicts that the operating ratio (output/capacity) for ethylene plants in the United States will be 80 percent in 1971 to supply 17.3 billion pounds (Anon., Chem. & Engr. News.,July 1, 1968).

Long-term projections of ethylene production are being revised continuously because of the increasing demands of this petrochemical intermediate as a raw material. For example, ethylene has replaced acetylene as a raw material choice in vinyl acetate monomer production. All producers agree that the availability of much cheaper ethylene on a large scale could bring about a 20 percent reduction in raw material costs, thus leading to the switchover from acetylene-based technology (Anon., Chem. & Engr. News.,August 12, 1968).

Effect of New Products on Growth

The projected petrochemical capacities obviously can change rapidly with the advent of new petrochemical products and new uses for existing products. Estimates indicate that approximately 500 new petroleum-based products are introduced to the market every year (Sherwood, 1963). Although the majority of recent products have limited consumption and short commerical life-span, many find an important market and add considerably to the annual growth of the petrochemical industry.

Based on projections which have been made to date, the petrochemical industry should continue to grow at least at its present rate. The introduction of new uses and products may even increase the industry's growth rate above its present level. In 1966, petrochemical production required the use of 650,000 barrels of petroleum daily, and in 35 years this requirement will be 12 million barrels per day (Sawyer, 1966). This expansion will present new and more complex problems in the area of water pollution control. This situation, coupled with more stringent pollution control regulations expected in the future, will necessarily require the industry to place more emphasis, attention, and capital investment toward solving these problems.

REFERENCES - CHAPTER II

1. Aalund, L., "Petrochemical Activity Hits a New High Around the World," The Oil and Gas Journal, v. 65, p. 108 (Sept. 4, 1967).

2. Anon., "Demand for Ethylene Worldwide Will Grow," Chem. & Engr. News, v. 46, n. 44, p. 34 (Oct. 14, 1968).

3. Anon., "Ethylene or Acetylene Route to Vinyl Acetate?" Chem. Engineering, v. 75, n. 17, p. 94 (Aug. 12, 1968).

4. Anon., "Ethylene Overcapacity Trend to Reverse in Next Three Years," Chem. & Engr. News, v. 46, n. 28, p. 15 (July 1, 1968).

5. Anon., "Huge Global Petroleum Gains Forecast," The Oil and Gas Journal, v. 64, p. 180 (May 9, 1966).

6. Anon., "Polypropylene Fiber Aims at Wider Market," Chem. & Engr. News, v. 46, n. 23, p. 24 (May 27, 1968).

7. Anon., "Propylene Demand: Up 50 Percent by 1973," Chem. & Engr. News, v. 46, n. 33, p. 26 (Aug. 5, 1968).

8. Anon., "Propylene Oxide Production May Grow 10 Percent This Year," Chem. & Engr. News, v. 46, n. 29, p. 12 (July 8, 1968).

9. Anon., The Petroleum Handbook, Shell International Petroleum Industry Co LTD. , 5th Edition, Balding and Mansell, Ltd. eds., London (1966).

10. Anon., "Toray Signs Up UOP for Toluene-Based Benzene, Xylenes Process," Chem. & Engr. News, v. 46, n. 16, p. 15 (April 15, 1968).

11. Anon., "What Puts Zip in Petrochemicals," Business Week, p. 40 (Dec. 17, 1966).

12. Conklin, H. L., "Water Requirements of the Carbon-Black Industry,"U S G S, Water Supply Paper 1330-B, U. S. Govn't. Printing Office, Washington, D. C. (1953).

13. McGrath, H. G., "Petrochemicals to Star '60's," The Oil and Gas J., v. 59, p. 129 (Nov. 20, 1961).

14. Noller, C. R., Textbook of Organic Chemistry, 2nd Edition, W. B. Sanders Co., Philadelphia, Pa. (1958).

15. Sawyer, F. G., "Best Picks for '66: Petrochemicals," Hydrocarbon Processing, v. 45, n. 1, p. 161 (Jan. 1966).

16. Sherwood, P. W., "First-Generation Chemicals Today," World Petroleum Annual Refinery Review, v. 35, n. 8, p. 61 (1964).

17. Sherwood, P. W., "Solvents and Plasticizers," Ind. and Engr. Chemistry, v. 54, n. 9, p. 35 (Sept. 1962).

18. Sherwood, P. W., "Whither Petrochemicals?" The Oil and Gas J., p. 73 (Dec. 16, 1963).

19. Stanley, H. M., The Petroleum-Chemicals Industry, Lecture Series 1963, No. 4, The Royal Institute of Chemistry (1963).

20. Stephenson, R. M., Introduction to the Chemical Process Industry, Reinhold Pub. Corp. New York (1966).

21. Stockton, J. R., Arbingast, S. A., Henshaw, R. C., Jr. and Dale, A. G., Water For The Future, Vol. II, Bureau of Business Research, The Univ. of Texas, Austin, p. 30 (1959).

22. Weiss, A. H., "Which Propylene Process Is Best?" Hydrocarbon Processing, v. 47, n. 4, p. 123 (April 1968).

CHAPTER III

PETROLEUM RAW MATERIALS

The first-generation petrochemicals are the initial stock in the synthesis of all petrochemical products and are produced from a variety of petroleum fractions. Principal fractions used for the preparation of primary petrochemical feedstocks include natural gas, refinery gas, natural gas condensate, light tops or naphtha, and heavy fractions such as fuel oil. The latter three fractions are obtained from the distillation of crude petroleum or crude oil. In some cases petrochemicals are produced directly from crude oil, particularly in Europe where the demand for naphtha is beginning to exceed the supply. The following section will briefly discuss these raw materials and the primary processes used to convert them to petrochemical feedstocks.

NATURAL GAS

Natural gas is probably the most desirable chemical feedstock in the United States since it contains a relatively small number of hydrocarbons and because it is readily available. Natural gas is available in two forms: "wet" gas which is separated from crude oil and "dry" gas which is unassociated with any other significant petroleum fraction. The "wet" natural gas is dissolved in the crude oil and is removed at the wellhead when the petroleum is brought to the surface. "Dry" natural gas, which is liquid under normal temperatures, comes to the surface under its own pressure and contains no petroleum.

Methane is the primary constituent of all natural gases and is usually combined with varying amounts of higher paraffins (Goldstein, 1958). Small amounts of hydrogen sulfide, nitrogen, and helium are also associated with some natural gases. Methane is important in the production of carbon black, hydrogen, synthesis gas, various chlorinated solvents, and acetylene. Acetylene is the basic constituent in the synthesis of several important organic compounds, but most of these can be produced from ethylene which is considerably cheaper.

Ethane, propane, butane, and pentane also commonly occur in natural gases. Propane, butane, and pentane can be separated in the liquid form by scrubbing the gas with a heavy petroleum fraction followed by distillation to obtain the absorbed liquids. Two other methods are also used. One involves compression and cooling of the natural gas and the other involves removal of the heavier hydrocarbons from the gas, then recycling it back into the ground where it picks up additional amounts of the heavier hydrocarbons (Stephenson, 1966). The natural gas liquids thus obtained are used for domestic heating purposes and for feedstocks in the petrochemical industry. Propane is used to prepare ethylene and propylene, the two principal olefins used for chemical synthesis.

Ethane also is separated from natural gas, and virtually all of this hydrocarbon produced is converted to ethylene. Natural gas is produced in enormous quantities in the United States, but only about three percent by volume is presently used in the preparation of chemicals (Anon., Shell, 1966). The remainder of this gas is used as fuel. In the future, liquified petroleum gases (LPG) obtained from natural gas should occupy a larger percentage of the feedstocks used for petrochemical production since large quantities are available at relatively low costs, particularly in the United States (Lewis, 1966). Increased industrial requirements for ethylene, for which ethane and propane are the most favored feedstocks, should require the use of more natural gas as the raw material for the petrochemical industry.

CRUDE PETROLEUM

Crude petroleum contains a great number of hydrocarbons, most of which can be classified in three categories: paraffins, naphthenes, and aromatics. The paraffins are straight-chain hydrocarbons ranging from methane to heavy waxes containing thousands of different isomers (Stephenson, 1966). Naphthenes are mostly derivatives of cyclopentane and cyclohexane. The aromatics present in crude petroleum are principally benzene related compounds. Varying quantities of sulfur, nitrogen, and oxygen are also found in crude oil. As expected, there are no olefins, diolefins, or acetylene present in crude petroleum since these are all quite reactive compounds.

In order to obtain useful products, the crude oil must be refined. It is during the refining processes that the fractions used for preparing the first-generation petrochemicals are obtained. The particular refining operations vary from one refinery to another, but the following general scheme will show how petrochemical raw materials are obtained.

Crude petroleum is first separated into six broad fractions by a primary distillation step. Most of the five-carbon and lighter hydrocarbons are removed in the first step, called stabilization, in which the crude is heated to about 300°F under a pressure of about 50 psig (Stephenson, 1966). After most of the gas is removed, the crude is heated to 600-800°F and distilled at atmospheric pressure. This distillation separates the crude, based on the boiling point, into an overhead fraction containing methane, ethane, and other gases; a bottom fraction of heavy residual oil; and 12 side streams which are removed from various heights of the column (Stephenson, 1966). The top gases, the light tops or naphtha, and the heavy bottom fractions are those used for the preparation of petrochemical feedstocks. The primary distillation of crude oil is schematically illustrated in Figure III-1.

REFINERY GASES

Following the distillation process, the gasoline fractions must be further refined prior to marketing. This refining consists of converting the straight-chain paraffins to branched-chain paraffins and the napthenes to aromatics. The branched-chain paraffins and aromatics are less prone to cause preignition in internal combustion engines and thus are more desirable for fuels. The processes used for this conversion vary somewhat, but all are based on the catalytic cracking of the gasoline fractions, which basically consists of splitting and rearranging hydrocarbon molecules using heat and pressure. It is extremely complex, but the primary reactions can be generally defined as follows (Stephenson, 1966).

$$\text{Long-chain Paraffin} \longrightarrow \text{Short-chain Paraffin} + \text{Olefin}$$

$$\text{Alkyl-Naphthene} \longrightarrow \text{Naphthene} + \text{Olefin}$$

$$\text{Alkyl-Aromatic} \longrightarrow \text{Aromatic} + \text{Olefin}$$

These equations indicate that considerable amounts of by-product olefins are formed during cracking operations. These olefins constitute what is known as refinery gas and provide an important source of ethylene and propylene. Some uncracked aliphatics, principally ethane and propane, are also present in the refinery gas. Ethylene/ethane, propylene/propane, and butylene/butane are recovered from the gases by distillation and adsorption (Anon., Shell, 1966).

The propylene recovered from refinery gas is generally considered adequate to meet the demands for petrochemical synthesis. However, chemical demand for ethylene and butylene far exceeds the supply of these compounds available from refinery cracking processes. Additional quantities of butylene and ethylene required by the industry must be supplied by pyrolysis of aliphatic compounds, including the ethane, propane, and butane from the refinery gases.

LIGHT TOPS

Another important source of petrochemical feedstock is light tops or naphtha which contains the lower paraffinic gasoline fractions. These fractions are unsuitable for blending fuels or for conversion to fuel hydrocarbons by catalytic reforming. Conversion of these fractions into olefins and diolefins is accomplished by cracking in the presence of steam (Anon., Shell, 1966). Naphtha is also important in the production of synthesis gas, particularly in Europe.

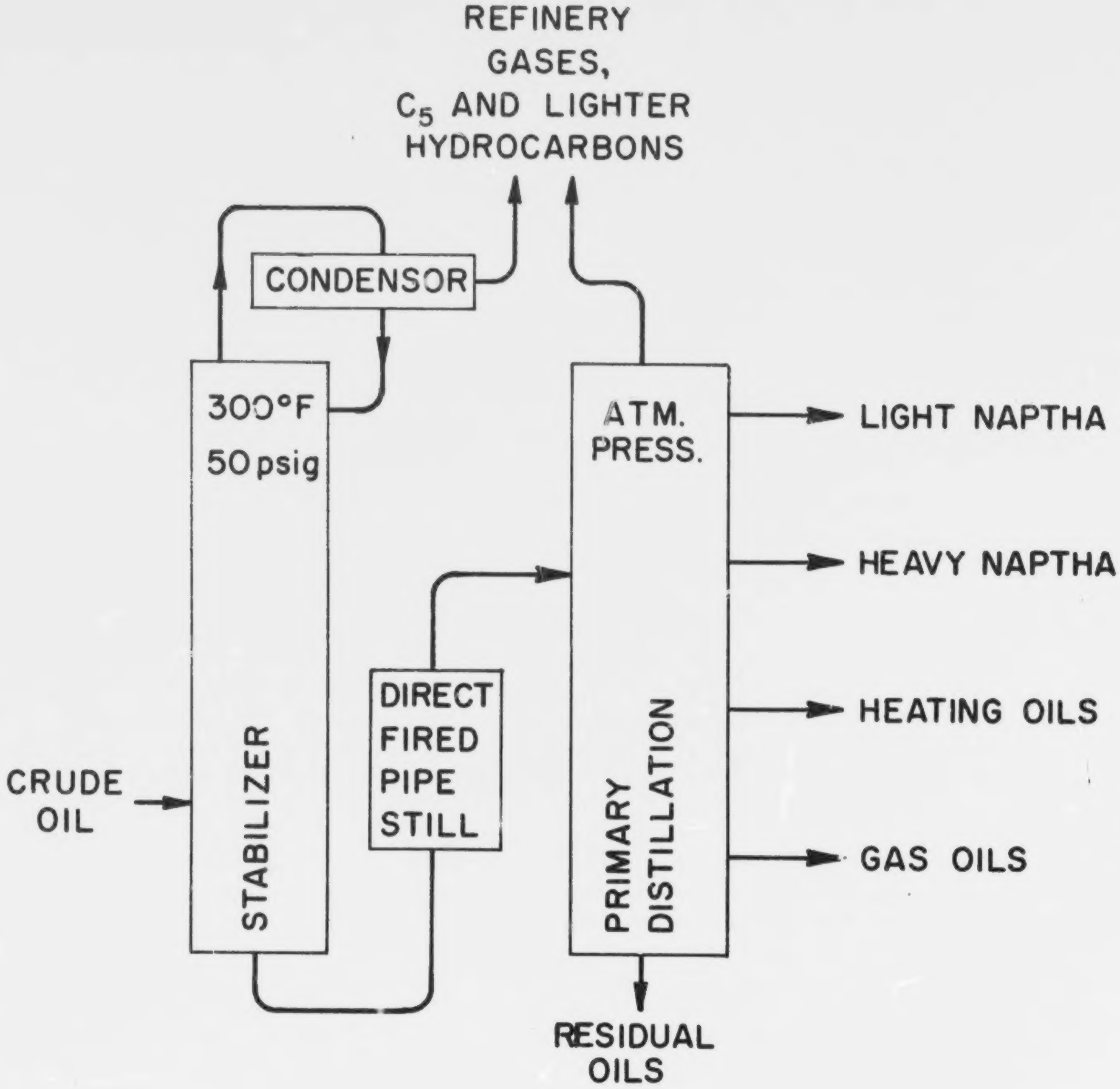

REFINERY GASES, C_5 AND LIGHTER HYDROCARBONS
CONDENSOR
300°F
50 psig
STABILIZER
CRUDE OIL
DIRECT FIRED PIPE STILL
ATM. PRESS.
PRIMARY DISTILLATION
LIGHT NAPTHA
HEAVY NAPTHA
HEATING OILS
GAS OILS
RESIDUAL OILS

FIGURE III-1

PRIMARY DISTILLATION OF CRUDE PETROLEUM

HEAVY FRACTIONS

The increasing demand for ethylene and butylene has required the petrochemical industry to look for additional sources. The heavy fractions such as fuel oils, which are obtained during the primary distillation of crude petroleum, and condensate from light gas and oils are finding an increasing market as the source for these two olefins and for other primary petrochemicals. Cracking these heavy fractions in the presence of steam results in the formation of olefins and diolefins which are the basic petrochemical feedstocks. Synthesis gas also can be produced by partially oxidizing the heavy fractions.

Unrefined petroleum is also being used directly in the production of petrochemical feedstocks, especially in Europe. European petrochemistry has been based on the light tops or naphtha produced during petroleum refining, but the increasing demand for this feedstock is beginning to create deficits. Methods have now been developed which can produce directly from crude oil many of the basic petrochemicals such as synthesis gas, acetylene, and ethylene. Crude oil, which is comparatively cheap, will probably be more widely used in the future as the basic source of European petrochemical production. It is doubtful that this will occur in the United States since other feedstocks which are more economical to process are more readily available.

AROMATICS FROM PETROLEUM

Certain petroleum fractions contain large, naturally occurring quantities or aromatics, with substantial amounts of these compounds also being formed during catalytic reforming operations. The increasing demand by the petrochemical industry for benzene has created a market for aromatics derived from petroleum and its fractions.

Several methods are used for extracting aromatics from these fractions. These methods include extractive distillation, liquid/liquid extraction, and adsorption on silica gel (Anon., Shell, 1966). Increasing emphasis is also being placed on the hydrodealkylation of branched chain aromatics, such as toluene, to produce benzene. This hydrodealkylation process also produces a xylenes stream which contains about 20 percent of ethylbenzene, an undesirable. An alternative route to hydrodealkylation has been developed which converts toluene to benzene plus a xylenes stream of only one percent ethylbenzene.

In addition to benzene, the aromatics which are used in significant amounts by the petrochemical industry include toluene and the three isomeric xylenes: ortho, meta, and para. Petroleum has now replaced coal and coke as the principal source of aromatic hydrocarbons. In 1962, petroleum accounted for 76.5 percent of all benzene production, 91.5 percent of toluene production, and 97.5 percent of all xylene production in the United States (Sherwood, 1964).

Presently, aromatics are being isolated only from the catalytic reformates and the petroleum fractions from the primary distillation procedure. Naphthas from catalytic cracking contain high percentages of aromatics, but the large amounts of olefins and sulfur present in these fractions prevent easy separation of the aromatics, thus making them undesirable as feedstocks for dealkylation (Stephenson, 1966). Most of the aromatics present in petroleum are not currently used for chemical production but instead go into gasolines to improve the octane rating. If the need arises, the petroleum industry could easily supply several times the present production of aromatics for the chemical industry.

REFERENCES - CHAPTER III

1. Anon., The Petroleum Handbook, Shell International Petroleum Co. Ltd., 5th Edition, Balding and Mansell, Ltd., eds., London,(1966).

2. Goldstein, R. F., The Petroleum Chemicals Industry, 2nd Edition, Spon, London (1958).

3. Lewis, N. J., "Natural Gas Liquids for Petrochemicals: How Big?" Hydrocarbon Processing, v. 45, n. 6, p. 195 (June 1966).

4. Sherwood, P. W., "First-Generation Chemicals Today," World Petroleum Annual Refinery Review, v. 35, n. 8, p. 61 (1964).

5. Stephenson, R. M., Introduction to the Chemical Process Industry, Reinhold Pub. Corp., New York (1966).

BLANK PAGE

CHAPTER IV

PETROCHEMICAL PROCESSES

A working knowledge of the principal production processes which constitute the major waste sources is required to understand adequately the complexities involved in petrochemical waste treatment. The petrochemical industry uses many variations of the chemical processes discussed herein, but the details of most of these special processes are proprietary. The principal wastewaters which are associated with most of these processes are generally known or can be deduced from the chemical operations which occur. The processes for primary, intermediate, and third generation petrochemicals are tabulated in Appendix I.

PRIMARY CONVERSION PROCESSES

The majority of petrochemical feedstocks are produced from crude petroleum. A heterogeneous mixture of many hydrocarbons, crude petroleum must be subjected to various fractionation and purification processes before it can be used in the production of petrochemical products. These preliminary processes constitute what is commonly known as petroleum refining. These refining processes differ among various refineries, but a generalized description is possible. Four methods are used to obtain the separation of individual hydrocarbons from crude oil. Combinations of methods are often used to produce the individual hydrocarbons of desired purity (Hatch, 1955).

Distillation

Three types of distillation are used, all involving separation of hydrocarbons by differential boiling characterizations. Distillation at a single pressure level separates compounds on the basis of molecular size, while alternate use of two pressures will separate molecular configuration.

The ease with which components of a mixture are separated by distillation processes is a direct function of the relative volatilities of the components. If two compounds boil at the same or approximately the same temperature, they are inseparable by ordinary distillation. However, artificial means may be used to increase the difference between the volatilities of two components, thus enabling them to be separated by distillation. Azeotropic and extractive distillation are the most commonly used of these processes.

In azeotropic distillation, a third component is added to a binary mixture of components having close boiling points. The third component forms an azeotrope with one or both of the components of the binary mixture, changing the relative volatility of each component and resulting in an increase in boiling points differences After distillation, the azeotrope-forming compound is removed from the distilled fraction either by washing with water or by partial immiscibility caused by lowering the temperature of the azeotrope.

Extraction

This process purifies the mixtures by using solvents which preferentially dissolve defined hydrocarbons. The hydrocarbons can be separated according to molecular orientation by using different solvents and different temperatures (extractive distillation).

Adsorption and Absorption

Various materials having selective preference for individual hydrocarbons or impurities can be used in combination or at different temperatures to isolate and purify hydrocarbon mixtures.

These materials operate by the mechanisms of adsorption, whereby a layer of solute molecules adheres onto a solid surface, or absorption in which there is an actual transfer of the solute molecules into the interstices of the absorbent.

Crystallization

By changing the pressure and temperature of a hydrocarbon mixture or by using specific solvents, certain components of the mixture can be crystallized and removed in a purified, solid form since the crystallization-recrystallization characteristics are an inherent property of a given compound.

The processes described are also used to isolate and purify many of the final petrochemical products after they are manufactured.

In the early developmental stages of the petrochemical industry, raw materials required were readily available as low-cost by-products from oil refining operations. There is now a trend toward so-called "vertical integration" in which manufacturers utilize all processes from the refining of the crude oil to the production of the final petrochemical product (Stephenson, 1966). Thus, the processes which were formerly associated with refineries are now being used at petrochemical complexes and contribute to the wastewater emissions from the industry.

The first step in production of petrochemicals is the separation of raw materials or feedstocks from crude petroleum. This process is known as primary distillation, and it separates the crude into six broad fractions or "cuts" which are still mixtures of various hydrocarbons, Figure III-1.

The fractions obtained from the primary distillation procedure are further refined by using one or more of the four separation processes. These processes separate the simple hydrocarbons which are used in petrochemical synthesis from the more complex hydrocarbons which are used in fuels and lubricants.

Many of the hydrocarbons present in the heavier fractions (gasoline, kerosene, residual oils) are made up of six or more carbon chain molecules. Catalytic cracking is used to break these long-chain hydrocarbons to six or less carbon chain compounds which constitute the principal feedstock of the petrochemical industry. The principal reaction in catalytic cracking is the rupture of a paraffin molecule resulting in one olefin molecule and one paraffin molecule each having fewer carbons than the original paraffin (Goldstein, 1958). Dehydrogenation occurs simultaneously with the cracking process, producing an olefin with the same number of carbons as the starting paraffin. These processes constitute the primary source of olefins for the petrochemical industry.

The flow of the petrochemical raw materials through the conversion processes is schematically described in Figure IV-1. Only the most commonly used of the many possible combinations of these processes are shown in the diagram.

Natural gas, also an important petrochemical feedstock, was not included in Figure IV-1 because the primary processing is considerably different from that of crude oil since the gas contains relatively few types of hydrocarbons. Separation of these hydrocarbons is normally carried out by using the same techniques as those employed to obtain the fractions from the primary distillation of crude petroleum.

Catalytic reforming processes are used to produce aromatics from naphthenes and branched-chain paraffins from straight-chain paraffins. The aromatics are removed from the product stream by separation processes similar to those used on crude oil. This is an important source of aromatics for use in the petrochemical industry.

SECONDARY CONVERSION PROCESSES

The primary conversion processes as defined herein consist principally of those processes which provide for the separation of the petroleum raw materials into the purified hydrocarbons used in the manufacture of petrochemical products.

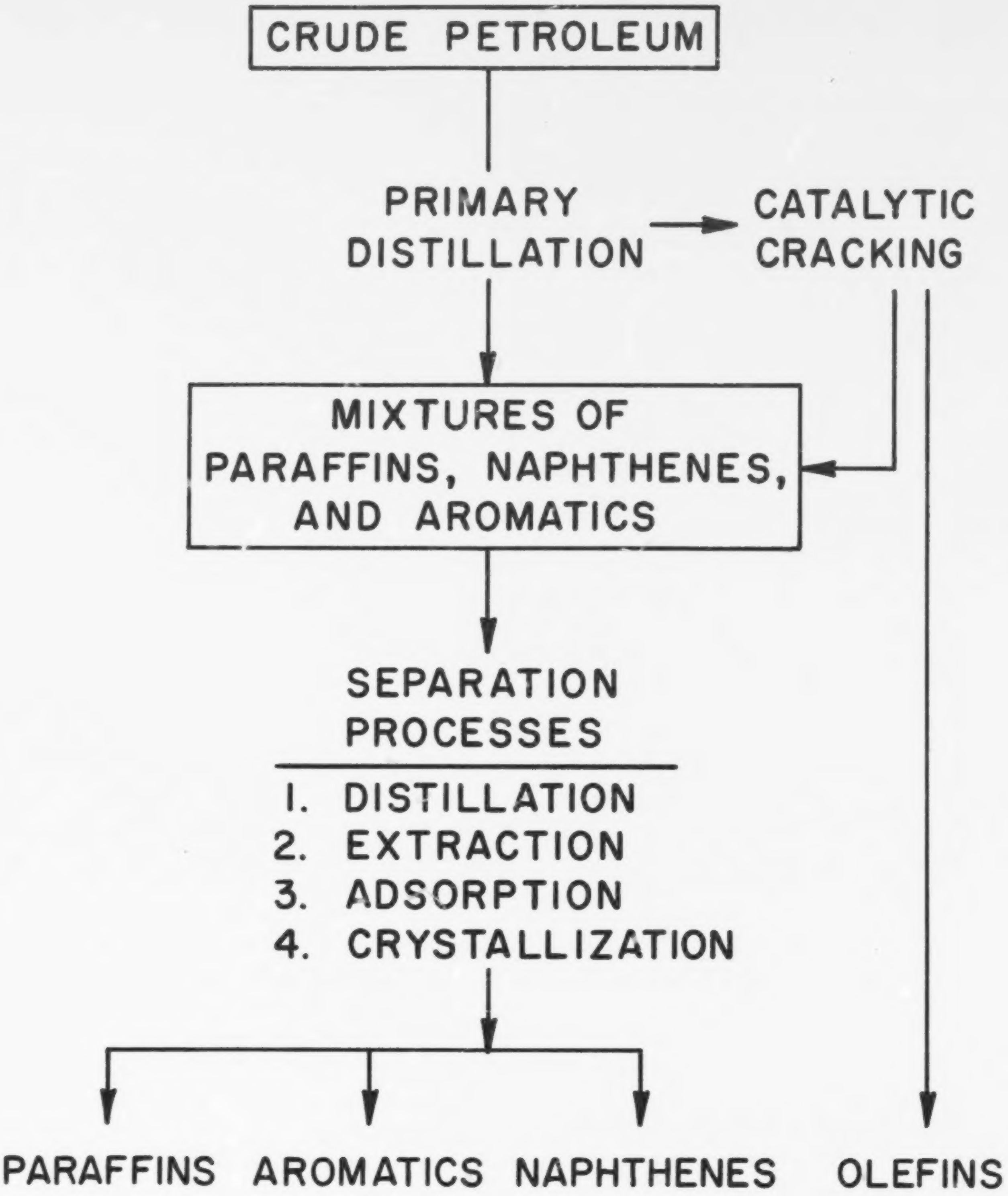

CRUDE PETROLEUM
PRIMARY DISTILLATION
CATALYTIC CRACKING
MIXTURES OF PARAFFINS, NAPHTHENES, AND AROMATICS
SEPARATION PROCESSES
1. DISTILLATION
2. EXTRACTION
3. ADSORPTION
4. CRYSTALLIZATION
PARAFFINS
AROMATICS
NAPHTHENES
OLEFINS

FIGURE IV-1
PRIMARY CONVERSION PROCESSES

Secondary conversion processes are used to convert the purified hydrocarbon feedstocks into the final product, exclusive of such final finishing operations as the molding of plastics from polymers, the manufacture of nylon fabrics, and other similar operations. Many of the purification processes used to separate petrochemical products following secondary processing are identical to the primary conversion processes previously discussed and need not be reiterated.

Secondary conversion processes comprise a variety of chemical reactions. These operations include oxidation, halogenation, hydrogenation, alkylation, isomerization, polymerization, nitration, sulfonation, hydrocyanation, and many combinations and variations of these chemical reactions. The secondary processes and the types of petrochemicals obtained from them are schematically shown in Figure IV-2. A brief description of each of the processes will help to identify the pollutants associated with petrochemical production and to locate the sources of these pollutants.

Before discussing secondary conversion processes, a brief definition of the terms "side-product" and "by-product" should be inserted. By-products are the inevitable result of the stoichiometry of a particular reaction, while side-products are those products formed by parallel reactions which compete with the primary reaction taking place. A more detailed discussion of these products will be given later.

Oxidation

Oxidation of propane and butane to various aldehydes, acids, and alcohols is one of the older petrochemical processes (Wright, 1959). Butane is the preferred raw material since it can be directly oxidized to acetic acid and butyl alcohols which are "high profit" chemicals (Hatch, 1955). The direct oxidation of paraffins is an economically competitive process because these oxygenated chemicals can be produced in one step, while the production of the same chemicals from olefins usually requires a minimum of two separate steps (Hatch, 1955). Another important direct oxidation product is adipic acid, a nylon monomer obtained by oxidizing a naphthene cyclohexane. A problem which must be coped with during the oxidation of paraffins is the multiplicity of by-products and side-products which are formed. These products must be separated from the primary product and sold or used in subsequent reactions. Another problem involves the loss of process carbon in the form of carbon monoxide and carbon dioxide.

The oxidation of aromatic hydrocarbons is usually accomplished by catalyzed reactions at temperatures considerably higher than those required for paraffin and naphthene oxidation. One characteristic inherent in aromatic oxidation is the usual formation of one-product rather than the primary and many side-products which are formed during paraffin oxidation. The most important industrial

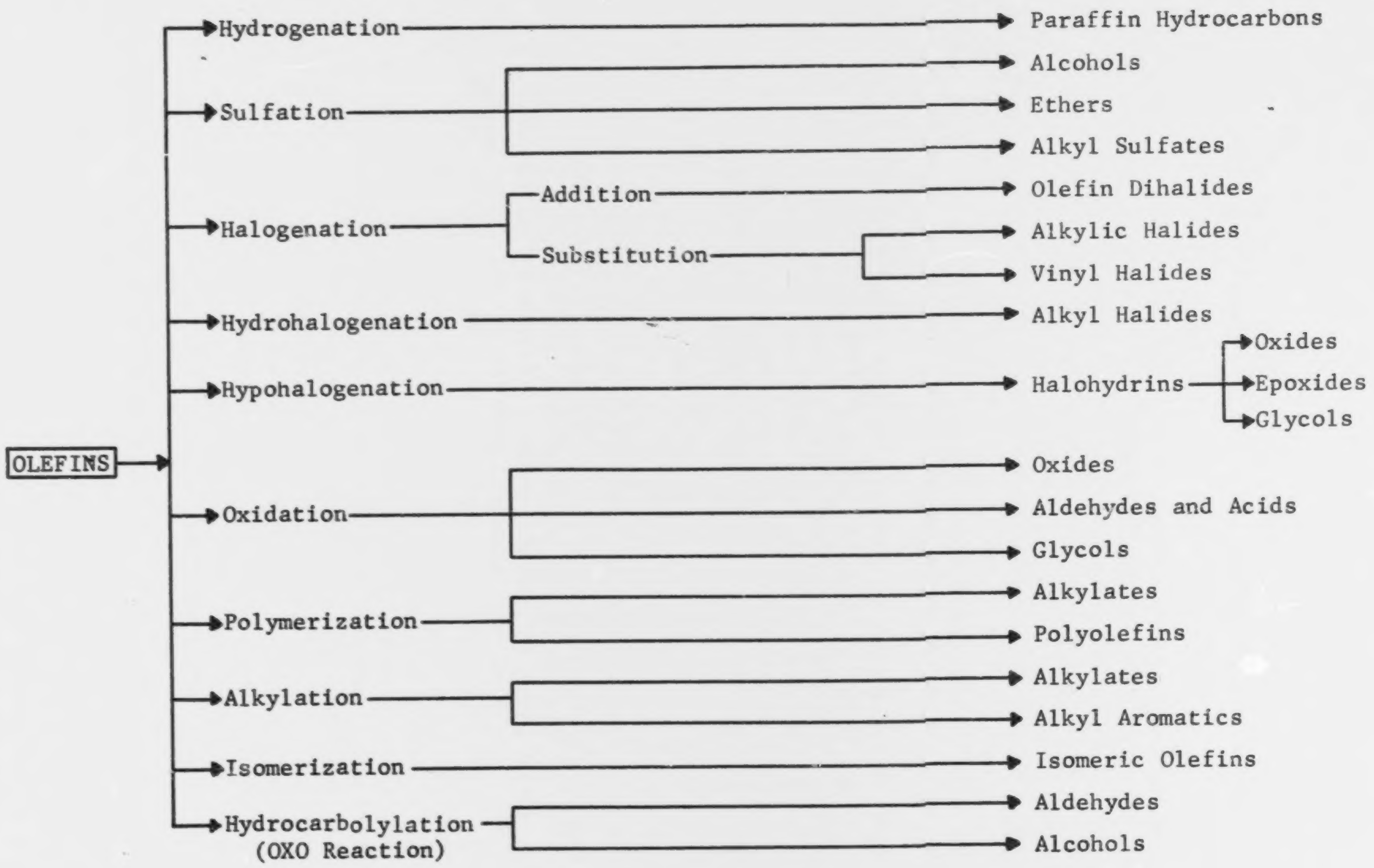

OLEFINS
Hydrogenation
Paraffin Hydrocarbons
Sulfation
Alcohols
Ethers
Alkyl Sulfates
Halogenation
Addition
Olefin Dihalides
Substitution
Alkylic Halides
Vinyl Halides
Hydrohalogenation
Alkyl Halides
Hypohalogenation
Halohydrins
Oxides
Epoxides
Glycols
Oxidation
Oxides
Aldehydes and Acids
Glycols
Polymerization
Alkylates
Polyolefins
Alkylation
Alkylates
Alkyl Aromatics
Isomerization
Isomeric Olefins
Hydrocarbolylation
(OXO Reaction)
Aldehydes
Alcohols

FIGURE IV-2

SECONDARY CONVERSTION PROCESSES

(Reference 2)

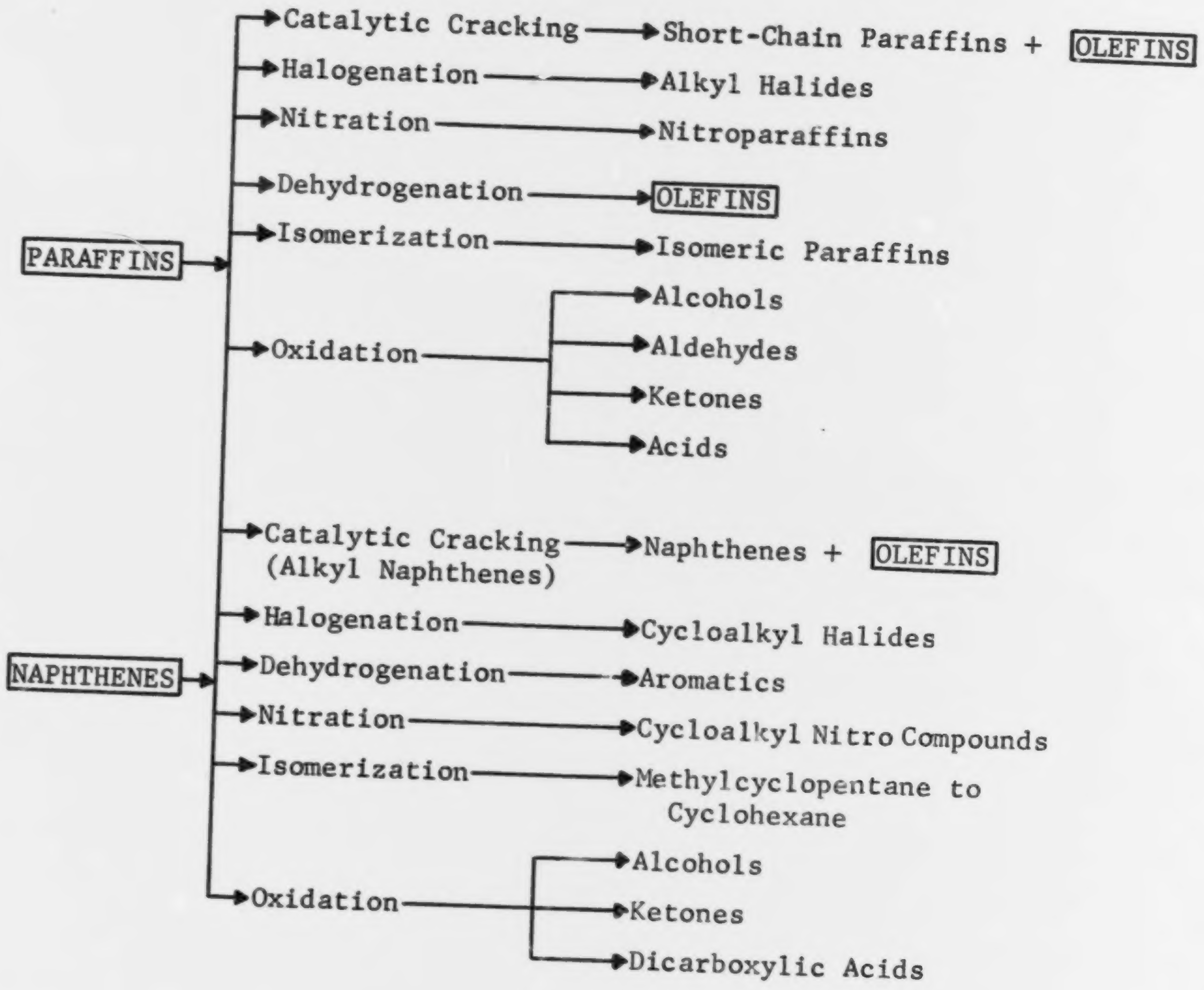

PARAFFINS
Catalytic Cracking
Short-Chain Paraffins + OLEFINS
Halogenation
Alkyl Halides
Nitration
Nitroparaffins
Dehydrogenation
OLEFINS
Isomerization
Isomeric Paraffins
Oxidation
Alcohols
Aldehydes
Ketones
Acids
NAPHTHENES
Catalytic Cracking (Alkyl Naphthenes)
Naphthenes + OLEFINS
Halogenation
Cycloalkyl Halides
Dehydrogenation
Aromatics
Nitration
Cycloalkyl Nitro Compounds
Isomerization
Methylcyclopentane to Cyclohexane
Oxidation
Alcohols
Ketones
Dicarboxylic Acids

FIGURE IV-2 (Continued)

SECONDARY CONVERSION PROCESSES

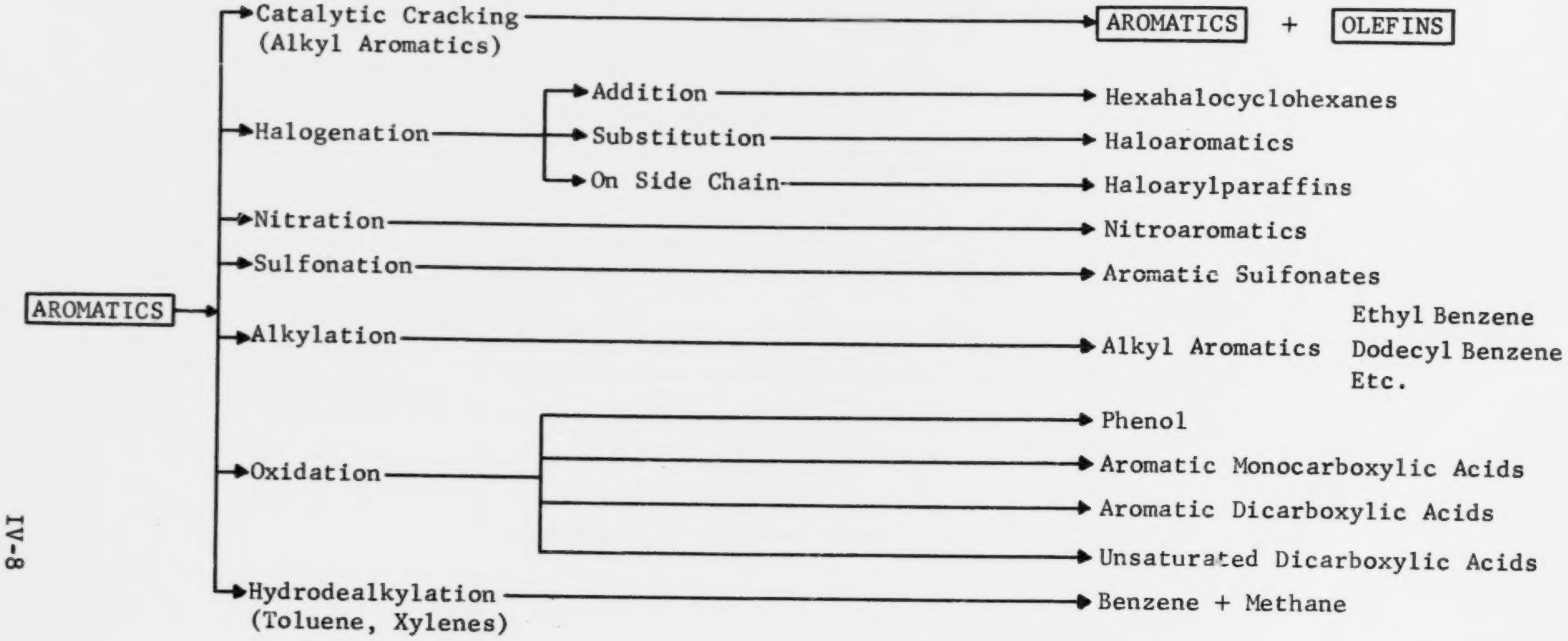

AROMATICS
Catalytic Cracking
(Alkyl Aromatics)
AROMATICS
+
OLEFINS
Halogenation
Addition
Substitution
On Side Chain
Hexahalocyclohexanes
Haloaromatics
Haloarylparaffins
Nitration
Nitroaromatics
Sulfonation
Aromatic Sulfonates
Alkylation
Alkyl Aromatics
Ethyl Benzene
Dodecyl Benzene
Etc.
Oxidation
Phenol
Aromatic Monocarboxylic Acids
Aromatic Dicarboxylic Acids
Unsaturated Dicarboxylic Acids
Hydrodealkylation
(Toluene, Xylenes)
Benzene + Methane

FIGURE IV-2 (Continued)

SECONDARY CONVERSION PROCESSES

reactions include the oxidation of benzene to maleic acid and anhydride, the manufacture of phenol and acetone from cumene and the formation of phthalic anhydride from orthoxylene. Other important aromatic oxidation products include benzoic acid, benzaldehyde, and terephthalic acid.

Probably the single most important petrochemical reaction, in terms of chemical tonnage produced, is the oxidation of ethylene to ethylene oxide. This direct oxidation of ethylene, using a selected catalyst, accounts for 85 percent of the ethylene oxide production in the United States. Another important olefin oxidation is the conversion of propylene to acrolein which can be further oxidized to glycerine. Direct oxidation of propylene is not economical due to the high yield of side-products.

Methane is oxidized to synthesis gas, a mixture of carbon monoxide and hydrogen, which is used in the manufacture of ammonia and methanol.

Hydration of olefins, which constitutes the addition of a water molecule to an olefin molecule, can also be considered as an oxidation process since oxygenated products are formed. The principal petrochemical products available by olefin hydration include ethanol from ethylene and acetaldehyde from acetylene.

Halogenation

Halogenation processes, principally chlorination, are also important petrochemical reactions. Except in the case of the olefins, chlorination is the only commercially important halogenation reaction. This is partly because chlorinated products presently have the largest economic market and partly because of the ease of performing the chlorination reaction compared to the other halogenation reactions. Olefins, however, will react directly with either bromine or chlorine at low temperatures, while under similar conditions iodine is unreactive and fluorine is too reactive (Hatch, 1955). The saturated fluorine compounds which are now widely used (Freon 12, Teflon) are obtained by reacting the appropriate chlorinated hydrocarbons with various fluorine compounds, particularly hydrofluoric acid, rather than by direct fluoridation.

Additional reactions can be performed using chlorine, hydrochloric acid, and hypochlorous acid. Brominated derivatives of olefins are also important commercially. These are the only types of halogenated products other than the chlorine compounds which are formed by direct halogen addition.

Processes which use the direct addition of a halogen to an olefin are characterized by an absence of by-product formation and a relatively rapid, complete reaction with no side-product formation

(Wright, 1959). Addition of chlorine to benzene is used in the production of hexachlorocyclohexane, which does occur in several isomeric forms. As a general rule, however, additional reactions do not result in significant by- and side-product formation.

The addition of a hydrogen halide to an olefin is known as hydrohalogenation. The only economically important process is hydrochlorination, the principal products being vinyl chloride and ethyl chloride. Ethyl chloride, obtained principally by the hydrohalogenation of ethylene, is used in the manufacture of tetraethyl lead.

Hypochlorination involves the addition of hypochlorous acid to olefins. This process is an important intermediate step in the production of epoxides and glycols. Ethylene chlorohydrin, produced by a hypochlorous acid-ethylene reaction, is easily dehydrohalogenated to give ethylene oxide. This is one of the primary sources of ethylene oxide. Hypochlorination processes are characterized also by low yields of side-products.

Nitration and Sulfonation

Paraffins and aromatics both can be nitrated; however, the nitrated aromatics have considerably more economic importance than the nitrated paraffins. Nitroparaffins are used primarily as solvents and as chemical intermediates. The nitration of paraffins results in the formation of many side-products with a simultaneous oxidation of the paraffin and the production of acids, ketones, aldehydes, alcohols, carbon dioxide, olefins, and water (Hatch, 1955).

The nitration of aromatic hydrocarbons is an extremely important industrial reaction. Aromatics react easily with nitric acid producing very little side-product formation and no ring oxidation. For example, nitrobenzene formation is 95 to 98 percent complete under the normal reaction conditions (Hatch, 1955). The addition of more than one nitro group to an aromatic ring is considerably more difficult because of the inactivation of the ring by the first nitration. When more than one nitration is made on the benzene ring, there will be a formation of the various product isomers, requiring additional separation processing to obtain the desired product.

Sulfonation is the addition of the sulfonic acid group ($-SO_3H$) to an organic compound and should not be confused with sulfation, which involves the addition of a sulfate ($-O-SO_3H$) group. In petrochemical production, paraffins and aromatics are the hydrocarbon groups which are commonly sulfonated. The only important commercial use of sulfonated paraffins is as surface active agents present in detergent products. Rigorous reaction conditions are required for the successful sulfonation of paraffins, resulting in by-product formation. Typical by-products include hydrogen chloride and sodium chloride.

Aromatics, particularly benzene, are easily sulfonated using sulfuric acid, oleum, or free sulfur trioxide (Hatch, 1955). Sulfonated aromatics are used in synthetic detergent manufacture, in dye manufacture, and in the manufacture of many other chemical products such as saccharin and phenol (Hatch, 1955).

Sulfonation of aromatics does not result in the formation of by-products although substituted aromatic isomers are formed. For example, all three sulfonated isomers of toluene are formed, the distribution of each being determined by the reaction temperature. Sulfonated alky aromatics provide the least expensive source of the most important component of detergents, the surface-active material.

Alkylation

The principal type of alkylation, Friedal-Crafts reactions, used by the petrochemical industry involves the addition of an olefin to an aromatic compound. The addition of alcohols and alkyl halides to aromatics, the dimerization of two olefins, and the reaction between an olefin and a paraffin are also known as alkylation (Hatch, 1955).

The most important alkylation reactions are those used in the production of various intermediate compounds from benzene, notably ethylbenzene, which is used in styrene production; cumene, which is used in the production of acetone and phenol; and dodecylbenzene, which is sulfonated and used in the production of surface-active agents (Wright, 1959). Many catalysts are used in these alkylation reactions, aluminum chloride being the most common. Alkylation of aromatics results in the production of few side-products; although in the manufacture of ethylbenzene, steps must be taken to prevent the formation of polyethylbenzenes (Stephenson, 1966). The production of cumene, resulting from the alkylation of benzene and propylene, is carried out in the presence of a solid phosphoric acid catalyst. However, formation of the by-product, diisopropylbenzene (DIPB), is unavoidable and undesirable. Originally this reaction was carried out in the presence of excess benzene to minimize this by-product formation, but this method was expensive because of the extra process equipment and benzene recovery system required. More recently, it has been determined that DIPB can be transalkylated with benzene and other catalysts to yield 90 percent cumene (Mita, and Kametaka, 1968). The alkylation of paraffins is important in gasoline production but not particularly significant in petrochemical production. A recent report claims that the modern alkylation process can produce alkylate of acceptable quality from an olefin feed of 100 percent propylene in the presence of a catalyst. Thus, this alkylating technique may become increasingly attractive as a propylene consumer (Vahlsing, 1968).

Dehydrogenation

Dehydrogenation is the removal of one or more hydrogen atoms from an organic molecule. The most important commercial dehydrogenation process is the formation of butadiene from n-butane and n-butylene. Small amounts of butadiene are produced during catalytic cracking, but the majority is formed by catalytic dehydrogenation. The most common process used is the Houdry process, using n-butane as the feedstock. Since the conversion process is incomplete, conventional adsorption and distillation processes are required to remove unreacted butane and butylene from the final product, butadiene. These unreacted hydrocarbons are then recycled through the process. This dehydrogenation process requires the use of catalysts, high reaction temperatures, and reduced pressure. An additional important dehydrogenation use is the dehydrogenation of ethyl-benzene to make styrene monomers.

Polymerization

Polymerization processing is presently one of the most active areas in petrochemistry. Some of the more common polymerization products include plastics of all types, resins used in adhesives and paints, fibers such as nylon and dacron, and elastomers known commonly as synthetic rubbers.

High molecular weight polymers, or macromolecules, are large molecules composed of two or more low molecular weight monomers. The polymer configuration can be linear, chain, or branched. The branched polymers may have their side chains joined by cross-links which form a three-dimensional or network polymer (Stephenson, 1966). The multiplicity of polymeric combinations possible make it impractical to discuss polymerization processes specifically, but the principles involved can be outlined in a general way.

Polymerization processes can be classified best in terms of the two mechanisms of polymer formation: step polymerization, which proceeds through the direct interaction of specific functional groups on the monomers, usually with the elimination of a small molecule such as water; or chain polymerization, which involves the reaction of "active centers" on the monomers with growth occurring only by the addition of single monomers to the chain.

The details of these polymerization processes depend on the type of polymer being produced, but all require various catalysts and other chemical additives in order to insure production of the desired end-product. The polymers can be either liquid or solid with widely varying chemical and physical properties.

Other Processes

Obviously, many other chemical reactions are important in petrochemical production. A brief description of the more important miscellaneous processes is desirable in order to fully explain the sources and types of potential air and water pollutants.

Ammonia is an extremely important petrochemical product, the largest single use for this compound being in the manufacture of nitrogeneous fertilizers. Ammonia is produced from the catalytic combination of nitrogen gas with hydrogen gas at high temperature and pressure. The hydrogen gas used in the reaction is obtained from synthesis gas, an important petrochemical intermediate. A number of different processes for ammonia production are used, their primary difference being the temperature, pressure, and catalyst employed. The most common catalyst used is iron.

Hydrocyanation, using hydrogen cyanide as a reactant was the process used to manufacture acrylonitrile, an important monomer used in acrylic fiber and plastics production. Even older processes used in acrylonitrile production involved the direct addition of hydrogen cyanide to acetylene or the addition of hydrogen cyanide to ethylene oxide, splitting off a molecule of water (Stephenson, 1966). Replacing the older process is a newer method using propylene and ammonia reactants instead of hydrogen cyanide. Hydrogen cyanide is also used in the manufacture of organic acids.

Hydrocarboxylation, more commonly known as the OXO reaction, can be used to produce aldehydes. This process combines an olefin with carbon monoxide and hydrogen in the presence of a cobalt catalyst to produce the desired aldehyde (Hatch, 1955). Hydrogenation is used to convert the aldehydes produced by the OXO process to alcohols and organic acids. The principal disadvantage of the OXO process is that the product stream usually contains a mixture of many isomers, thereby handicapping its use as an intermediate for other petrochemical products (Stephenson, 1966). The products from the OXO reaction contain cobalt and iron carbonyls which must be separated and, in the case of cobalt, reused. Hydrogenation reactions use various catalysts including nickel and cobalt, and the product streams will contain these catalysts as well as small amounts of unreacted aldehydes.

Sulfation processes are also used to produce alcohols from olefins. The olefin is absorbed in sulfuric acid using acid concentrations ranging from 50 percent to 98 percent and temperatures in the range of 0° to 80°C. Ethers, polymers, and dialkyl sulfates are three side products formed, but this formation can be adequately controlled to reduce the total quantity produced (Hatch, 1965). The alkyl hydrogen sulfates formed during sulfation are then hydrolized to produce alcohols and dilute sulfuric acid which are separated by distillation procedures.

PROCESSES AS WASTE SOURCES

The multiplicity of processes used and products produced by the petrochemical industry indicates the scope and complexity of the petrochemical waste problem. If one considers all of the process combinations used by the industry, it is obvious that many types of air and water pollutants can result. The principal petrochemical processes and the wastes which might be expected to emanate from them are listed in Table IV-1.

A general review of major pollutants in the petrochemical industry reveals that many of them can be traced to sources common to most petrochemical processes. The characteristics of these sources are listed below (Wright, 1959).

By-Product Formation

In some cases the by-products formed may have commercial value, but usually this is not the case and more often these products present waste disposal problems.

Side-Product Formation

Side-products are compounds which are formed by reactions competing with primary reactions during petrochemical processing. These side-products are often isomers of the principal product. They may also be reaction products from impurities present in the feedstock or other extraneous reactions which might occur during the petrochemical process. These side-products range in composition from pure chemical compounds which might have some commercial value to unrecognizable tars and complexes. Unlike by-products, side-product formation often can be controlled by modifying the conditions of the chemical reaction (Wright, 1959).

Incomplete Reactions

In petrochemical practice, no reaction ever goes to completion. The many reactions used by the industry vary markedly in their efficiency ranging from almost 100 percent completion to only 20 percent of completion. In other words, the product stream from any petrochemical process will contain varying quantities of the feed chemical which must be separated from the final product. Often, especially in cases of low conversion efficiency, the feed chemical is recycled through the process; but in some cases, it is not economically justifiable and they are disposed of as wastes.

Mechanical and Accidental Losses

Every mechanical or physical operation is subject to various losses, including accidental leaks, spills, and explosions, or losses caused by human error (Wright, 1959). Mechanical losses include fluid losses from valves, defective seals in compressors and

TABLE IV-1

PETROCHEMICAL PROCESSES AS WASTE SOURCES

Process	Source	Pollutants
Alkylation: Ethylbenzene		Tar, Hydrochloric Acid, Caustic Soda, Fuel Oil
Ammonia Production	Demineralization	Acids,Bases
	Regeneration,Process Condensates	Ammonia
	Furnace Effluents	Carbon Dioxide, Carbon Monoxide
Aromatics Recovery	Extract Water	Aromatic Hydrocarbons
	Solvent Purification	Solvents - Sulfur Dioxide, Diethylene Glycol
Catalytic Cracking	Catalyst Regeneration	Spent Catalyst, Catalyst Fines (Silica,Alumina Hydrocarbons, Carbon Monoxide, Nitrogen Oxides
	Reactor Effluents and Condensates	Acids, Phenolic Compounds, Hydrogen Sulfide Soluble Hydrocarbons, Sulfur Oxides, Cyanides
Catalytic Reforming	Condensates	Catalyst (particularly Pt, Mo), Aromatic Hydrocarbons, Hydrogen Sulfide, Ammonia
Crude Processing	Crude Washing	Inorganic Salts, Oils, Water Soluble Hydrocarbons
	Primary Distillation	Hydrocarbons, Tars, Ammonia, Acids, Hydrogen Sulfide
Cyanide Production	Water Slops	Hydrogen Cyanide, Unreacted Soluble Hydrocarbons

TABLE IV-1 (Continued)

PETROCHEMICAL PROCESSES AS WASTE SOURCES

Process	Source	Pollutants
Dehydrogenation		
Butadiene Prod. from n-Butane and Butylene	Quench Waters	Residue Gas, Tars, Oils, Soluble Hydrocarbons
Ketone Production	Distillation Slops	Hydrocarbon Polymers, Chlorinated Hydrocarbons, Glycerol, Sodium Chloride
Styrene from Ethylbenzene	Catalyst	Spent Catalyst (Fe, Mg, K, Cu, Cr, Zn)
	Condensates from Spray Tower	Aromatic Hydrocarbons, including Styrene, Ethyl Benzene, and Toluene, Tars
Desulfurization		Hydrogen Sulfide, Mercaptans
Extraction and Purification		
Isobutylene	Acid and Caustic Wastes	Sulfuric Acid, C_4 Hydrocarbon, Caustic Soda
Butylene	Solvent and Caustic Wash	Acetone, Oils, C_4 Hydrocarbon, Caustic Soda, Sulfuric Acid
Styrene	Still Bottoms	Heavy Tars
Butadiene Absorption	Solvent	Cuprous Ammonium Acetate, C_4 Hydrocarbons, Oils
Extractive Distillation	Solvent	Furfural, C_4 Hydrocarbons
Halogenation (Principally Chlorination)		
Addition to Olefins	Separator	Spent Caustic
Substitution	HCl Absorber, Scrubber	Chlorine, Hydrogen Chloride, Spent Caustic, Hydrocarbon Isomers and Chlorinated Products, Oils

TABLE IV-1 (Continued)

PETROCHEMICAL PROCESSES AS WASTE SOURCES

Process	Source	Pollutants
	Dehydrohalogenation	Dilute Salt Solution
Hypochlorination	Hydrolysis	Calcium Chloride, Soluble Organics, Tars
Hydrochlorination	Surge Tank	Tars, Spent Catalyst, Alkyl Halides
Hydrocarboxylation (OXO Process)	Still Slops	Soluble Hydrocarbons, Aldehydes
Hydrocyanation (for Acrylonitrile, Adipic Acid, etc.)	Process Effluents	Cyanides, Organic and Inorganic
Isomerization in General	Process Wastes	Hydrocarbons; Aliphatic, Aromatic, and Derivative Tars
Nitration		
Paraffins		By-Product Aldehydes, Ketones, Acids, Alcohols, Olefins, Carbon Dioxide
Aromatics		Sulfuric Acid, Nitric Acid, Aromatics
Oxidation		
Ethylene Oxide and Glycol Manufacture	Process Slops	Calcium Chloride, Spent Lime, Hydrocarbon Polymers, Ethylene Oxide, Glycols, Dichloride
Aldehydes, Alcohols, and Acids from Hydrocarbons	Process Slops	Acetone, Formaldehyde, Acetaldehyde, Methanol, Higher Alcohols, Organic Acids

TABLE IV-1 (Continued)

PETROCHEMICAL PROCESSES AS WASTE SOURCES

Process	Source	Pollutants
Acids and Anhydrides from Aromatic Oxidation	Condensates Still Slops	Anhydrides, Aromatics, Acids Pitch
Phenol and Acetone from Aromatic Oxidation	Decanter	Formic Acid, Hydrocarbons
Carbon Black Manufacture	Cooling, Quenching	Carbon Black, Particulates, Dissolved Solids
Polymerization, Alkylation	Catalysts	Spent Acid Catalysts (Phosphoric Acid), Aluminum Chloride
Polymerization (Polyethylene)	Catalysts	Chromium, Nickel, Cobalt, Molybdenum
Butyl Rubber	Process Wastes	Scrap Butyl, Oil, Light Hydrocarbons
Copolymer Rubber	Process Wastes	Butadiene, Styrene Serum, Softener Sludge
Nylon 66	Process Wastes	Cyclohexane Oxidation Products, Succinic Acid, Adipic Acid, Glutaric Acid, Hexamethylene, Diamine, Adiponitrile, Acetone, Methyl Ethyl Ketone
Sulfation of Olefins		Alcohols, Polymerized Hydrocarbons, Sodium Sulfate, Ethers
Sulfonation of Aromatics	Caustic Wash	Spent Caustic

TABLE IV-1 (Continued)

PETROCHEMICAL PROCESSES AS WASTE SOURCES

Process	Source	Pollutants
Thermal Cracking for Olefin Production (including Fractionation and Purification)	Furnace Effluent and Caustic Treating	Acids, Hydrogen Sulfide, Mercaptans, Soluble Hydrocarbons, Polymerization Products, Spent Caustic, Phenolic Compounds, Residue Gases, Tars and Heavy Oils
Utilities	Boiler Blow-down	Phosphates, Lignins, Heat, Total Dissolved Solids, Tannins
	Cooling System Blow-down	Chromates, Phosphates, Algicides, Heat
	Water Treatment	Calcium and Magnesium Chlorides, Sulfates, Carbonates

pumps, leaks in various units, etc. Volatile hydrocarbons are often lost to the atmosphere via relief valves and improperly sealed storage facilities. Storm water runoff from the processing areas often contains pollutants which have seeped from various process units.

The losses of volatile hydrocarbons from valves, fittings, etc., is significant in both quantity of hydrocarbon lost and in air pollution created in the plant area. Calculations of the hydrocarbon losses from an ethylene plant are shown in Table IV-2 (Mencher, 1967). This example shows that mechanical losses can be quite significant, with the total being much higher if the leakage of nonvolatile hydrocarbons was included. Obviously the degree of maintenance practiced and condition of equipment at a particular plant would be reflected in the mechanical and accidental losses incurred by the plant.

No attempt was made to characterize the waste streams in Table IV-1 with respect to individual chemical pollutants or to wastewater management parameters such as chenical or biochemical oxygen demand. The wastes associated with petrochemical processing will be completely characterized in the following chapter.

The actual operations which are the principal contributors of water pollutants in the petrochemical industry are listed below (Mencher, 1967).

a) Steam distillation
b) Steam cracking
c) Steam stripping
d) Product washing with water, caustics, and acids
e) Barometric condensing of steam-driven prime movers
f) Catalyst regeneration
g) Boiling and cooling water blow-downs
h) Rainwater runoff from processing areas
i) Cleaning operations (Process)
j) Partial pressure reduction with dilution steam
k) Transfer and storage operations
l) Crude petroleum desalting
m) Solvent processes
n) Still tars from distillation processes
o) Product and feedstock drying

One or more of these operations are used in each of the primary and secondary conversion processes and usually are the prime contributors of water-borne pollutants.

All of the foregoing factors are involved in the waste discharges from a large petrochemical complex. The actual quantities

TABLE IV-2

A CALCULATION OF HYDROCARBON LOSSES FROM PROCESS EQUIPMENT IN A 500 MM LB/YR ETHYLENE PLANT

(Reference 3)

Emission Source	Loss Factor[1]	Emission	Quantity (lb/day)
Valves	0.15 lb/day/valve	4,500 valves x 0.15 =	675
Pumps (mech. seal)	3.2 lb/day/seal	150 pumps x 3.2 =	480
Compressors (centrif., mech. seal)	3.2 lb/day/seal	10 comp. x 2 x 3.2 =	64
Compressors (recip., packed seal)	5.4 lb/day/seal	1 comp. x 5.4 =	5
Cooling water	6.0 lb/MM gal(circulated)	$\frac{50{,}000 \text{ gpm} \times 60 \times 24 \times 6}{1{,}000{,}000} =$	430
Process drains and wastewater separators	150 lb/1,000 bbl cap.	$\frac{20{,}000 \text{ bbl} \times 150}{1{,}000} =$	3,000
Blow-down	100 lb/1,000 bbl cap.	$\frac{20{,}000 \text{ bbl} \times 100}{1{,}000} =$	2,000
Relief valves (operating vessels)	2.9 lb/day/valve	400 valves x 2.9 =	1,150
Relief valves (storage tanks)	0.6 lb/day/valve	14 tanks x 2 x 0.6 =	17
Storage tanks (floating roof)	4.8 lb/day/1,000 bbl cap.	$\frac{500{,}000 \text{ bbl} \times 4.8}{1{,}000} =$	2,400

TABLE IV-2 Continued)

A CALCULATION OF HYDROCARBON LOSSES FROM PROCESS EQUIPMENT IN A 500 MM LB/YR ETHYLENE PLANT

Emission Source	Loss Factor(1)	Emission	Quantity (lb/day)
Storage tanks (floating roof) (VP 1.5 lb/sq in)	1.7 lb/day/1,000 bbl cap.	$\frac{5{,}000 \text{ bbl} \times 1.7}{1{,}000} =$	9
Miscellaneous losses	10 lb/day/1,000 bbl cap.	$\frac{20{,}000 \text{ bbl} \times 10}{1{,}000} =$	200
Total calculated hydrocarbon emission		$\frac{10{,}430}{20{,}000 \times 250} = 0.21\%$	10,430 lb/day
Weight % loss on plant feed(2)			

(1) These loss factors are applicable to plants practicing extensive hydrocarbon control.

(2) The range of emissions from hydrocarbon processing plants may range from 0.1 to 0.6 percent by weight of plant throughout. The lower value calculated here is applicable to an area as Los Angeles County where stringent control is practiced.

and types of pollutants discharged by a plant will depend on several factors, including the type of raw petroleum feedstock used by the plant, the products manufactured, the quantity of in-plant control, and the maintenance, condition, and types of processing equipment used. Marginally efficient processes may still be used in older plants, resulting in the production of more side-products which are evident in the plant wastewater. In general, however, the rapid growth and active competition within the petrochemical industry reduces the importance of this factor as a waste source.

REFERENCES - CHAPTER IV

1. Goldstein, R. F., The Petroleum Chemicals Industry, 2nd Edition, Spon, London (1958).

2. Hatch, L. F., The Chemistry of Petrochemical Reactions, Gulf Pub. Co., Houston, Texas (1955).

3. Mencher, S. K., "Change Your Process to Alleviate Your Pollution Problem," Petro/Chem Engineer, p. 21 (May,1967).

4. Mita, Y., and Kametata, N., "Up Cumene Yield With Transalkylation," Hydrocarbon Processing, v. 47, n. 10, p. 122 (Oct. 1968).

5. Stephenson, R. M., Introduction to the Chemical Process Industries, Reinhold Pub. Corp., New York , (1966).

6. Wright, E. R., "Secondary Petrochemical Process as Waste Sources," Sew. and Ind. Wastes, v. 31, n. 5, p. 575 (May 1959).

7. Vahlsing, D. H., "HF Alkylation Gets Propylene Feed," Hydrocarbon Processing, v. 47, n. 9, p. 245 (Sept. 1968).

CHAPTER V

CHEMICAL AND PROCESS RELATED CLASSIFICATION OF WASTES

The petrochemical industry is extremely diversified in both the processes used and the materials produced, and the widely fluctuating characteristics of the wastewaters discharged from the industry reflect this diversity. It can be expected that most of the chemicals used in the manufacture of these products will be present in the aqueous effluents from the industry, making it extremely difficult to define or predict an average effluent from the petrochemical industry. However, most of the unit processes used in the industry are relatively similar, making it possible to predict the general nature of the pollutants from any given unit process.

Relating the general characteristics of a wastewater to the individual unit processes, the effluent characteristics for any given combination of petrochemical processes can be approximated. These estimations provide a basis for designing effluent segregation systems, in-plant pretreatment systems, and final treatment schemes for petrochemical wastewaters (Beychok, 1967).

Principal pollutional characteristics of petrochemical wastes will be defined in accordance with the unit process from which these wastes are discharged. The volume and concentration of these pollutants are as important as their inherent characteristics, but much more difficult to predict. The concentration of any given pollutant in a waste stream is dependent on the qualities of waterused in the process. For example, a petrochemical plant practicing extensive reuse of cooling water and minimum usage of stripping steam would, for a given quantity of pollutant, have a higher effluent concentration of the pollutant than a plant discharging the same total quantity of the pollutant but in a greater volume of water.

The one method of predicting the characteristics of a waste stream discharged from a given unit process is to relate the quantities of pollutants produced to the unit quantity of feedstock utilized or product manufactured by the process. A given unit process using a particular feedstock should produce a fixed quantity of pollutant per unit of feedstock utilized. These data can be statistically correlated for a particular unit process, thereby providing a basis for accurately predicting quantities of pollutants associated with the process. However, most of the published literature does not include sufficient information to characterize the waste by feedstock quantities utilized or products processed. Often the effluent flow rates are also excluded so that total pollutant quantities from a process cannot be calculated.

Many of the unit processes used in the petrochemical industry are also important in petroleum refining. The characteristics of these refining wastes are well documented (Beychok, 1967), and a detailed discussion will not be included in this report. The most important unit processes used by the petrochemical industry and their respective effluents are listed in Table IV-1. In some cases, for example, nylon manufacture, a combination of several unit processes, are listed. These processes normally will be combined in the same order for production. It can be seen from Table IV-1 that the effluent streams carrying the pollutants come from a relatively small number of sources. A brief discussion of each of these effluent streams will indicate the sources, nomenclature, and type of wastes which might be expected.

COOLING WATER

Cooling water often contains organic contaminants because of pipe leakage which may result in oil contamination. Also some organic materials are frequently added along with the chemicals used to control corrosion, scale formation, etc. Inorganic contamination of the water may become a serious waste problem since recirculated cooling water will tend to concentrate dissolved solids with the blowdown from such a system containing high dissolved solids concentration. Cooling water is often used to dilute toxic organic wastes to biologically treatable levels of concentration. Algicides and bacteriocides which may possibly restrict or inhibit subsequent biological treatment of the combined wastewater are sometimes added to cooling water.

PROCESS EFFLUENTS

Most of the highly polluted waste streams in a petrochemical plant originate from process areas. This category includes condensed steam from stripping operations, wash waters from process drum cleaning operations, water formed or eliminated during various reactions, and other in-process sources. A variety of pollutants are found in these wastewaters, including any or all of the chemicals present in the feedstocks, products, by- and side-products, and spent catalytic materials. Many of the compounds present in the effluents from unit petrochemical processes are indicated in Table IV-1. The pollutional characteristics of some typical process effluents will be shown subsequently.

The terminology used by the industry for the various process waste streams gives an approximate indication of the source and composition of each effluent. Steam is used for stripping during distillation operations and as a diluent in catalytic and thermal cracking (Beychok, 1967). The condensed steam is known as "condensate" which distinguishes it from other process wastes. Wastes containing relatively large amounts of hydrogen sulfide are usually referred to as "sour" water or sour condensates because of their unpleasant odor. Phenols or "phenolic wastes" are also common, particularly in the effluents from cracking operations.

Solvent Processes

Numerous solvent processes are utilized in petrochemical production to purify the chemical feedstocks, intermediates, and products used and manufactured by the industry, and are commonly found in aqueous waste streams discharged from processes using them. Additional solvents may find their way into wastewater through accidental leakage and solvent spills. Since the solvents used by the petrochemical industry in most instances are expensive, it is doubtful that large quantities of the commonly used solvents will be found in waste streams, but even low concentrations of many solvents used by the industry have deleterious biological effects. In this case it may be necessary to remove the solvent completely by pretreatment prior to biological treatment of the waste stream. Many of the solvents used by the petrochemical industry are similar to those used in petroleum refining.

Caustic Washes

Caustic washes utilizing aqueous sodium hydroxide solutions are frequently used in petrochemical processes and are sources of the various spent caustic streams cited in Table IV-1. Sodium hydroxide solutions are used to extract from process streams various acidic contaminants such as hydrogen sulfide, mercaptans, phenols, thiophenols, and organic acids (Beychok, 1967). Most spent caustic streams can therefore be expected to contain some or all of these compounds in the forms of sodium salts and unreacted sodium hydroxide as well as small quantities of the process product and feed chemicals.

Caustic washes are also used to recover unreacted acidic chemicals in such processes as chlorination, sulfation, sulfonation, polymerization, oxidation, and other processes utilizing or forming acidic compounds not desired in the product stream. The caustic washes from secondary petrochemical processes usually will not contain large amounts of sulfur compounds since most of these are removed by the preliminary refining processes.

Acidic Wastes

Petrochemical processing also involves the use of various acid washes to remove basic materials from product streams. Acid washes are often used also in removing contaminants from various phenolic product streams such as those emanating from phenolic resin manufacture. Acid process effluents also are present in refining and petrochemical operations, notably alkylation processing.

Phenolic spent caustics are usually neutralized with mineral acids (H_2SO_4, HCl) or flue gases containing SO_2 or CO_2, releasing an acidic, oily effluent consisting predominantly of phenolic compounds and referred to as "sprung acid" (Beychok, 1967). Acid sludges are also produced by various heavy oil treatment processes.

Washing and Scrubbing Operations

Caustic and acid washings are often followed by clear water rinses to remove all traces of the washing compounds. Off-gases from various units also are scrubbed with water to remove contaminants. Wash waters usually will contain pollutants similar in nature but smaller in concentration to those found in the preceding spent caustic or acid washes categories.

Crude Petroleum Desalting

The desalting of crude oil is primarily a petroleum refinery process and is important only in petrochemical plants which include primary processing of crude oil feedstocks. It is, however, a significant source of pollutants. Water present in crude oil may range in volume from 0.1 percent to 2.0 percent of the total. The effluent water will contain a high salt concentration and considerable oils and may exert a rather high oxygen demand. In a refinery the desalter effluents often contribute a significant portion of the total refinery biochemical oxygen demand (Beychok, 1967). This effect would probably occur less often in a petrochemical plant but if such a stream were present, the high salt concentration could raise the salinity of the plant effluent significantly. Desalter wastes often contain other contaminants such as abrasive sediments, arsenic, and vanadium organometal compounds (Beychok, 1967).

Other Sources

Other possible processing operations which may contribute pollutants include spillage of petrochemicals during transport or storage operations and runoff from processing areas. Spent catalytic material may find its way into aqueous waste streams and often can be a serious pollutant in terms of biological toxicity, even though it may be present only in small quantities.

CHEMICAL CLASSIFICATION OF PETROCHEMICAL WASTES

The vast number of chemicals and products manufactured by the petrochemical industry makes a complete listing of every compound which might be present in any petrochemical waste effluent impractical. However, the principal classes of chemicals which might be expected to emanate from various unit processes can be presented. The following discussion will separate the chemicals into two general classifications, inorganic and organic, with each of these divisions subdivided as required.

Inorganic Compounds

Inorganic chemical pollutants may be conveniently classified under two general subdivisions, metals and nonmetals.

Metals - Most of the metals associated with petrochemical effluents are catalytic materials from various unit processes. These metals often are associated with complex organic materials found in tars and other residues. Some of the more commonly used metallic catalysts are aluminum, platinum, molybdenum, iron, and chromium. The processes from which spent metallic catalyst pollutants might be expected are catalytic cracking, catalytic reforming, dehydrogenation, alkylation, isomerization, and polymerization. Other metals which also might be used as catalysts are nickel, cobalt, and copper.

Another source of copper in wastewater is the cuprous ammonium acetate solution used in the extraction and purification of butadiene. A similar cuprous solution is used to remove carbon monoxide from synthesis gas in preparation for ammonia synthesis (API, Vol. III.,1958). In both of these processes, a solution containing a mixture of cuprous and cupric ions is formed. This solution has an intense blue color, and the copper concentration is sufficient to be toxic. These solutions are reused and ordinarily are not allowed to escape from the process; however, accidental spills and leakages may occur in small amounts. Although most of the metals used as catalysts have a high economic value and are recovered, others, for example aluminum chloride, used in isomerization and treating processes, are usually discharged into the waste stream.

Anti-corrosion, algicidal, and bactericidal chemicals commonly composed of chromium and copper compounds, added to cooling and boiler waters are additional sources of metal pollutants. Zinc has been used also as a biocide to prevent undesirable growth of microorganisms in cooling towers. These chemicals represent a potential source of toxic materials and could have a deleterious effect on the performance of a biological treatment system.

Non-metals - Non-metallic inorganic pollutants are present in various petrochemical process effluents. In terms of total quantity, the sodium salts present in spent caustic streams are probably the most significant.

The sodium is frequently combined with sulfates, sulfites, and sulfides. Various quantities of unreacted sodium hydroxide are present in the spent caustics. Much of the sodium in phenolic spent caustics will be combined with phenols, cresols, and xylenols. Crude oil desalter effluents contain large quantities of sodium usually in the form of sodium chloride. Wash waters also contain various sodium salts.

Calcium hydroxide is an important caustic washing agent, particularly in chlorination processes. Spent caustic from processes using this material consists principally of calcium chloride, which is also present in desalter effluents in significant concentrations.

Sulfur compounds are some of the most important inorganic pollutants present in petrochemical effluents and many sulfur compounds have undesirable odors. Hydrogen sulfide and mercaptans contain the most reduced form of sulfur and have particularly objectionable odors; they are usually present in condensates and spent caustics from primary conversion and refining processes. Sulfates are present in the spent caustic from alkylation processes as is sulfuric acid, the acid stream being comprised of 85 percent to 90 percent sulfuric acid (Beychok, 1967). Sulfuric acid is also used as a solvent in various extraction processes and will appear in the process effluents. Sulfonates are found in spent caustic streams from aromatic sulfonation processes. Sulfur also can be associated with phenolic compounds in the form of thiophenols, which are often present in the condensates from catalytic cracking processes. Sulfur dioxide is found in gases from combustion processes and it is also found in waste from aromatic extraction processes where the SO_2 is used as a solvent.

Cyanide, present as both hydrogen cyanide and organocyanides, is found in some effluent streams and are particularly significant because of their toxic nature. Condensates from catalytic cracking units and process effluents from hydrocyanation reactions used in the production of intermediate chemicals for nylon manufacture contain cyanides.

Chlorides are present in crude desalter effluents and certain spent caustic streams previously discussed. Hydrochloric acid is found in the effluents from some chlorination processes and appears as a spent catalyst in alkylation process wastes.

Phosphates and polyphosphates are used for corrosion control in cooling and boiler waters. Phosphoric acid is used as a catalyst in polymerization, alkylation, and isomerization processes, and the spent acid catalyst may be found in process effluents if it is not segregated for separate disposal.

Potassium and magnesium also are found in effluents from certain unit processes. Potassium hydroxide is used as a caustic wash in some refinery operations. Magnesium and calcium salts are present in the waste sludge from cooling water treatment processes.

Ammonia, usually present as ammonium sulfide, is an important pollutant in condensates from refining processes. Nitric acid, another nitrogen-containing compound, may be present in wastes discharged from aromatic nitration processing.

Organic Compounds

The organic compounds present in petrochemical wastes are probably the most important pollutants in terms of both quantity and pollutional effects on biological environment. Organics in petrochemical effluents are far more diverse in their characteristics than inorganics. Only the classes of organic compounds commonly found in petrochemical effluents will be included in this discussion. The effluent from a specific unit process often is so complex that it can be characterized only in a general sense.

Hydrocarbons - Wastewaters containing hydrocarbon contaminants can emanate from any process utilizing hydrocarbon feedstocks. They are most common in condensates and caustic wastes from primary conversion processes.

Three general classes of saturated hydrocarbons are found in petrochemical wastes - aliphatics, aromatics, and cyclic aliphatics or naphthenes. The chemical characteristics of these hydrocarbon groups have been discussed. Saturated aliphatic hydrocarbons are practically insoluble in water; therefore, relatively low concentrations of these compounds are normally present in process wastewaters. The high volatility of the aliphatic hydrocarbons containing chain lengths of five carbon atoms or less also tends to keep the concentrations of these compounds in process effluents at low levels. The cyclic aliphatic compounds have chemical and physical properties similar to the aliphatic hydrocarbons. The aromatic hydrocarbons although relatively insoluble are considerably more soluble and less volatile than the other saturated hydrocarbons. Significant quantities of aromatic hydrocarbons are therefore an important constituent of process wastes from petrochemical processes in which aromatics are utilized or formed. Complex aromatic compounds such as naphthalene are also found in process effluents, particularly in effluents from refining processes. It should be mentioned that many saturated hydrocarbons are very difficult to degrade biologically.

The principal unsaturated hydrocarbons used in the petrochemical industry are the olefins: ethylene, propylene, and butylene ; and the alkyne, acetylene. These compounds are considerably more soluble than the saturated hydrocarbons but will seldom be found in process effluents in unreacted forms because of their high reactivity. The double bond and triple bond compounds will enter into additional reactions with many reagents, producing a variety of chemical products which will be discussed under other classifications. Small amounts of butadiene are occasionally found in the effluents from the polymerization of copolymer rubber (Dougan and Bell, 1951).

Other important types of hydrocarbons which can be found in petrochemical effluents are the mixed aliphatic-aromatic hydrocarbons. These compounds can be combinations of alkanes and aromatics such as toluene and xylene or unsaturated hydrocarbons and aromatics such as styrene. Ethyl benzene, which is used to manufacture styrene, is produced by alkylating benzene. Toluenes and xylenes are produced during the catalytic refoming and cracking of crude petroleum and are usually dealkylated to benzene. The effluents from dealkylation processes may contain these compounds. Since the aliphatic-aromatic hydrocarbons also are relatively insoluble in water, low concentrations of these compounds may be expected in wastewater streams.

Substituted Organic Compounds - Most of the organic compounds found in petrochemical effluents will be substituted organics or hydrocarbons which have had one or more of the hydrogens substituted by other functional groups. Most of the secondary petrochemical processes involve the rearrangement of hydrocarbon molecules and the addition of various reagents to them. These substituted organics can find their way into the various process effluents by any of the methods previously discussed. The following discussion will describe the various classes and characteristies of these substituted organics.

a. organic acids and their salts - Organic acids are defined as those organic compounds which can serve as proton donors. Although many organic compounds fit this description, the term organic acid is usually reserved for those compounds containing a carboxyl group consisting of two oxygen atoms, one carbon atom, and one ionizable hydrogen atom. The sulfonic acid group will be discussed later. The polar nature of the carboxylic acids makes those acids with four or less carbon atoms extremely water soluble so that high concentrations of these compounds may be found in process wastewaters coming in contact with them. The long-chain organic acids are considerably less soluble in water. The effect of organic acids on wastewater treatment systems is twofold. Their acidity tends to lower the pH of the effluent; and most of them are quite biodegradable, giving the waste a high potential oxygen demand. Organic acids can be found in waste streams in the free form or combined with various cations (Na, K, Ca) as a salt.

The most common carboxylic organic acids found in petrochemical wastes are probably formic and acetic acids which occur in the effluents from various oxidation processes. Nylon manufacture is the source of the following organic acids: succinic acid, adipic acid, and glutaric acid. Other organic acid sources are listed in Table IV-1.

The acid anhydrides are derivatives of organic acids which contain two oxygen atoms connected by two double bonds to two carbon atoms which, in turn, are connected to each other by another oxygen atom. The remaining single bonds on each of the two carbons are connected to an organic molecule, either aliphatic or aromatic. The anhydrides are relatively insoluble in water, and only small quantities should be expected in wastewater streams. The two most important anhydrides are both aromatics, phthalic anhydride and maleic anhydride, and are used in the manufacture of polymers. Aliphatic acid anhydrides are used to synthesize certain esters.

b. alcohols - The alcohols are organic compounds containing a hydroxyl group consisting of one hydrogen and one oxygen atom. The hydroxyl group can be joined to any alkyl or substituted alkyl group, giving the alcohol its prominent physical characteristics. The hydroxyl group is highly polar, making alcohols with chains of four or less carbon atoms highly water soluble. Longer chain alcohols tend to exhibit the properties of the less polar aliphatic portion of the molecule and are only slightly soluble. Alcohols will be found in effluents discharged from oxidation processes, in the form of by-products from nitration and sulfation processes, and in the form of solvents in solvent applications.

The most common alcohols found in the petrochemical industry include the simple alcohols such as methanol, ethanol, propanol, isopropanol; the butanols and other longer chained alkylalcohols; alkyl alcohol which contains a double bond; polyhydroxy alcohols, which include the glycols; and the cyclic aliphatic alcohol, cyclohexanol. The glycols are also used as solvents to extract aromatics from hydrocarbon mixtures (Beychok, 1967). Processes which might produce wastewaters containing alcohols are listed in Table IV-1.

c. aldehydes and ketones - Both aldehydes and ketones are characterized by the presence of the carbonyl group consisting of an oxygen atom attached to a carbon atom by a double bond. Aldehydes and ketones have similar physical properties primarily attributable to the carbonyl group, are relatively volatile, and those with four or less carbon atoms are very soluble in water.

Aldehydes often are present in effluents discharged from oxidation and paraffin nitration processing. Ketones are formed in the same processes and are often used as solvents in extraction and purification processes. Formaldehyde and acetaldehyde are the most common alkyl aldehydes, but many wastes will also contain the higher aldehydes in complex mixtures. Acrolein is an unsaturated aldehyde which occurs as a by-product in acrylonitrile manufacture and as an intermediate in a new process for manufacturing glycerol (Stephenson, 1966).

The most common ketones are acetone and methyl ethyl ketone. Acetone is present as a by-product in oxidation processes, and methyl ethyl ketone is a solvent used in a variety of extraction and purification processes.

d. esters - Esters are organic compounds formed by the reaction between an alcohol or phenol and a mineral or organic acid. Esters with five or fewer carbon atoms are quite soluble in water. Several common esters in petrochemical processing are vinyl acetate, ethylene diacetate, and methyl formate (Gloyna and Malina, 1962). The primary pollutional effect of esters is the creation of an oxygen demand due to their biodegradability. The lighter esters are also quite volatile and can impart an odor to wastewater; however, the odors of esters usually are considered pleasant.

e. ethers - Ethers are organic compounds which contain an oxygen atom bound to two carbon atoms. Ethers can be aromatic, aliphatic, or a combination of the two. They are nonpolar and therefore relatively insoluble in water. These compounds are quite volatile, their boiling points being comparable to those of alkanes with the same number of carbon atoms. The most common ethers produced in petrochemical processes are diethyl ether and isopropyl ether. Ethers occur as by-products during the sulfation of olefins during alcohol production.

Epoxides are an important class of organics which are closely related to ethers. Epoxides are highly reactive and will rarely be found in significant quantities in wastewaters. The most important epoxides are ethylene and propylene oxide, which are used in many petrochemical syntheses.

f. halogenated hydrocarbons - Halogenation reactions play an important role in petrochemical processing. Chlorine is the most commonly used halogen. These processes result in the formation of many chlorinated by-products and side-products which are discharged in the process effluents. Several classes of chlorinated hydrocarbons can be identified by the processes from which they are discharged.

Substitution reactions produce as side-products chlorinated isomers or higher chlorinated hydrocarbons which are slightly soluble in water and have an intermediate toxicity (Wright, 1959). Methyl and ethyl chlorides, chloroform, carbon tetrachloride, vinyl chloride, and propylene chloride are examples of substitution reaction products.

The addition of a halogen to an olefin is characterized by an absence of by-product formation. Chlorinated hydrocarbons from these processes are only slightly soluble and exhibit intermediate toxicity (Wright, 1959). Another important addition product is benzene hexachloride, which is used as an insecticide.

Hypochlorination reactions produce chlorohydrins which are highly toxic but are normally hydrolyzed prior to discharge in the process effluent. The hydrolyzed form is nontoxic and readily biodegradable.

Chlorinated hydrocarbons are also used as solvents and as cleaning fluids and may find their way into wastewaters from these sources.

g. nitrogenated compounds - There are several different types of nitrogenated organic compounds which may be found in petrochemical effluents.

The amines are alkyl or aryl compounds which contain a nitrogen atom. They are characterized by the appreciable basicity. The aliphatic amines are more basic than ammonia, while the aromatic amines are considerably less basic. Amines with six or less carbon atoms are water soluble, and the aromatic amines are usually extremely toxic. Monoethanolamine and diethanolamine are important solvents which are used to remove hydrogen sulfide and carbon dioxide from gas or liquid petrochemical streams. These amine treating units are sources of aqueous effluent containing amines. Aliphatic and aromatic amines also can originate from processes manufacturing or utilizing these compounds - hexamethylene diamine, for example, appears in the effluent from nylon manufacture.

Nitriles, or organic cyanides, consist of a nitrogen atom bound to a carbon atom by a triple bond constituting the cyanide group. Nitriles can be either aliphatic or aromatic and yield the corresponding alkyl or aryl acids when hydrolyzed. Acetonitrile is used as a solvent to extract butadiene from mixed four-carbon hydrocarbons (Beychok, 1967). Urea is a weakly basic compound which forms salts with acids. It will hydrolyze to ammonia and carbon dioxide in the presence of acids, bases, or through microbial action. It is also used in the manufacture of urea-formaldehyde resins, which are important in the manufacture of molded plastics.

Amides, derivatives of organic acids and ammonia, are soluble in water and will hydrolyze in the presence of acids or bases to produce ammonia and the corresponding acids.

h. phenolic compounds - Phenol consists of a benzene molecule with one of the hydrogen atoms substituted by the hydroxyl group. Cresols and xylenols, the other phenolic compounds which are common in petrochemical wastes, differ from phenol in that each has one or more alkyl groups connected to the benzene nucleus.

Phenol is relatively soluble in water, but some phenolic compounds are considerably less soluble. The solubilities of several phenolic-like compounds are presented in Figure V-1. Phenols are more acidic in nature than the alcohols; they will form salts with aqueous hydroxides, and aqueous mineral acids will reconvert these salts to free phenols. These reactions are used as the basis for treating petrochemical streams with caustic washes to remove the phenolic contaminants. The majority of phenolic pollutants in petrochemical effluents are found in spent caustics used in the primary conversion processes, principally in the catalytic and thermal cracking of petroleum.

i. organic sulfur compounds - There are several important organic sulfur compounds which often appear in petrochemical effluents, of which sulfonic acids, either aromatic or aliphatic, are an important class. The sulfonic acid group consists of one sulfur atom, three oxygen atoms, and a hydrogen atom and is generally indicated as $-SO_3H$. Sulfonic acids are distinguished from the esters of sulfuric acid by the direct bonding of the sulfur atom to a carbon atom in the organic molecule rather than the bonding of the oxygen atom to the carbon atom, as is the case with esters. Sulfonic acids are highly polar and, therefore, more water soluble than any other organic compound. Because of this high solubility, sulfonic acid salts constitute the most common surface-active material used in detergent manufacture. Sulfonic acids undergo all reactions typical of organic acids, including salt formation, esterification, and amide formation. Sulfonic acids and their salts will occur in effluents from sulfonation processes and detergent manufacture.

Mercaptans are foul-smelling organic sulfur compounds which contain a sulfhydryl group consisting of a sulfur atom and a hydrogen atom bound to an organic molecule by a single carbon-sulfur bond. These compounds are also known as thiols, and most of their chemical and physical properties are similar to alcohols though considerably more acidic in nature. Thiols are either aliphatic or aromatic, the most common aromatic thiol being known as thiophenol. Considerable quantities of thiols, particularly thiophenol, are present in some crude petroleum stocks. Such crudes must be treated with caustic washes to remove these compounds since they can poison catalysts used in subsequent petrochemical processing. These sulfur compounds will, therefore, be present in spent caustic streams from the primary refining processes and in the effluents from catalytic and thermal cracking of petroleum.

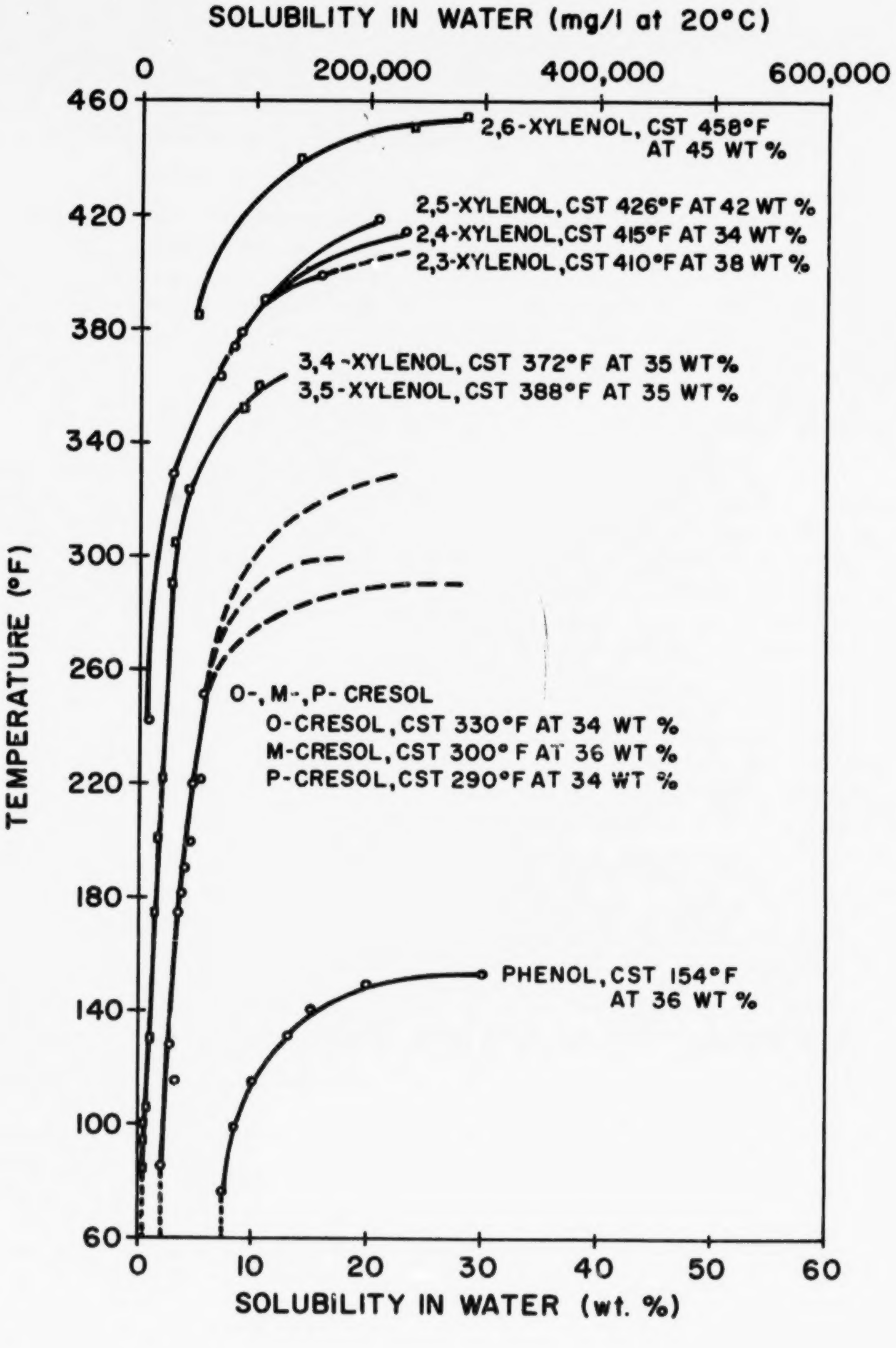


FIGURE V-1

SOLUBILITY OF PHENOLIC COMPOUNDS IN WATER

(Reference 4)

Miscellaneous Organics - The classes of organic contaminants previously listed include those which are common to several important unit petrochemical processes and, as a rule, might be expected in effluent streams. There are many compounds of miscellaneous origin which cannot be simply categorized, but which are too important to go unmentioned.

Wastes from many polymerization processes may contain small amounts of the polymer or constituent being produced. For example, butyl rubber scraps are present in process effluents from butyl rubber polymerization and finishing processes. Polyethylene, perchloroethylene, ABS, latex emulsions, and various vinyl polymers might also be found in process wastewaters. Most of the polymers are very insoluble in water and are essentially inert to biological action.

Cokes and tars are complex organic wastes which are discharged from the bottoms of distillation units. Cokes are formed in high temperature treating processes and during catalyst regeneraation. These complex organics may contain significant quantities of spent metallic catalysts, some having been previously discussed. Tars and cokes are insoluble in water and normally are not amenable to treatment by biological methods.

Furfural is a heterocyclic aldehyde which contains an oxygen atom within the carbon ring. It is used as a solvent in several extraction processes, including the extraction of butadiene from four-carbon hydrocarbons and the removal of polycyclic aromatics from oils (Beychok, 1967).

Various complex oils are present in the effluents from many unit processes. In aqueous process effluents, these oils may exist in the free state or as emulsions. Some oils are forced as byproducts during polymerization and other processing. An example of this type of oil is the "green oil" formed during acetylene hydrogenation and butadiene manufacture from butylenes. Other oils are simply mixtures of high molecular weight hydrocarbons.

REFERENCES - CHAPTER V

1. Anon., Manual on Disposal of Refinery Wastes, Vol. III, Chemical Wastes," American Petroleum Institute, New York (1958).

2. Anon., "Petrochemicals Face New Challenge," Business Week, no. 1618, p. 56 (Sept. 3, 1960).

3. Anon., Standard Methods for the Examination of Water and Wastewater, American Public Health Assoc., New York, N. Y., 12th ed. (1965).

4. Beychok, M. R., Aqueous Wastes from Petroleum and Petrochemical Plants, John Wiley & Sons, London (1967).

5. Chambers, C. W., Tabak, H. H. and Kabler, K. W., "Degradation of Aromatic Compounds by Phenol-Adapted Bacteria," J. WPCF, v. 35, n. 12, p. 1517 (Dec. 1963).

6. Cherry, A. B., Gabaccia, A. J. and Senn, H. W., "The Assimilation Behavior of Certain Toxic Organic Compounds in Natural Water," Sew. and Ind. Wastes, v. 28, n. 9, p. 1137 (Sept. 1956).

7. Dickerson, B. W., Campbell, C. J. and Stankard, M., "Further Operating Experiences on Biological Purification of Formaldehyde Wastes," Proc. 9th Ind. Waste Conf., Purdue Univ., p. 331 (1954).

8. Dougan, L. D. and Bell, J. C., "Waste Disposal Pit Synthetic Rubber Plant," Sew. and Ind. Wastes, v. 23, n. 2, p. 181 (Feb. 1951).

9. Eckenfelder, W. W., Jr., Lecture Series Prepared for Manufacturing Chemists Assoc., The Univ. of Texas, Austin (1967).

10. Eckenfelder, W. W., Jr., Ford, D. L. and Burleson, N. K., Unpublished Report (July 1968).

11. Elkin, H. F., "Condensates, Quenches, Wash Waters as Petrochemical Waste Sources," Sew. and Ind. Wastes, v. 31, n. 7, p. 838 (July 1959).

12. Englebrecht, R. S., Gandy, A. F., Jr. and Cederstrand, J. R., "Diffused Air Stripping of Volatile Waste Components of Petrochemical Wastes," J. WPCF, v. 33, p. 134 (Feb 1961).

13. Ford, D. L. and Eckenfelder, W. W., Jr., Unpublished Report (March 1968).

14. Ford, D. L. and Gloyna, E. F., Unpublished Report (Jan. 1967).

15. Ford, D. L. and Gloyna, E. F., Unpublished Report (Feb. 1967).

16. Ford, D. L. and Gloyna, E. F., Unpublished Report (May 1967).

17. Ford, D. L. and Gloyna, E. F., Unpublished Report (July 1967).

18. Gandy, A. F., Jr. and Englebrecht, R. S., "The Stripping of Volatile Compounds," Proc. 15th Ind. Waste Conf., Purdue Univ., p. 224 (1960).

19. Gandy, A. F., Jr., Englebrecht, R. S. and Turner, B. G., "Stripping Kinetics of Volatile Components of Petrochemical Wastes," J. WPCF, v. 33, p. 382 (1961).

20. Cloyna, E. F. and Burleson, N. K., Unpublished Report (March 1968).

21. Gloyna, E. F. and Malina, J. R., "Petrochemical Wastes Effect on Water," Ind. Water & Wastes, pt. 1, Sept. - Oct. 1962, p. 2, Nov. - Dec. 1962, pt. 3, Jan. - Feb. 1963, pt. 4, March - April, 1963.

22. Heukelekian, H. and Rand, M. C., "Biochemical Oxygen Demand of Pure Organic Compounds," J. WPCF, v. 27, p. 1040 (1955).

23. Ludzack, F. J. and Ettinger, M. B., "Chemical Structures Resistant to Aerobic Biological Stabilization," J. WPCF, v. 32, p. 1173 (1960).

24. Martin, J. M., Kincannon, C. B. and Bishop, J. L., "Ultraviolet Determination of Total Phenols," J. WPCF, v. 39, n. 1, p. 21 (Jan. 1967).

25. Mencher, M. R., "Minimizing Waste in the Petrochemical Industry," Chemical Engineering Progress, v. 63, n. 10, p. 80 (1967).

26. Nemerow, N. L., Theories and Practices of Industrial Waste Treatment, Addison-Wesley Pub. Co., Inc., Reading, Mass. (1963).

27. Noller, C. R., Textbook of Organic Chemistry, 2nd Edition., W. B. Sanders Co., Philadelphia, Pa. (1958).

28. Remy, E. D. and Lauria, D. T., "Disposal of Nylon Wastes," Proc. 13th Ind. Waste Conf., Purdue Univ., p. 596 (1958).

29. Senate Reports, Water Requirements for Pollution Abatement, Select Committee on National Water Resources, 86th Congress Committee Print No. 9 (1960).

30. Stephenson, R. M., Introduction to the Chemical Process Industry, Reinhold Pub. Corp., New York (1966).

31 Van Hall, R. E., Safranko, J. and Stenger, V. A., "Rapid Combustion Method for the Determination of Organic Substances in Aqueous Solutions," Analytical Chemistry, v. 35, p. 315 (1963).

32. Willard, N. H., Merritt, L. L., and Dean, J. A., Instrumental Methods of Analysis, Van Nostrand, Princeton, N. J. (1965).

33. Wilson, I. S., "The Treatment of Chemical Wastes," Waste Treatment, Isaac, P. C. G., ed., Pergamon Press, London, p. 206 (1960).

34. Wright, E. R., "Secondary Petrochemical Processes as Waste Sources," Sew. and Ind. Wastes J., v. 31, n. 5, p. 575 (May 1959).

CHAPTER VI

WASTE POLLUTIONAL EFFECTS AND THEIR CHARACTERIZATION

The multitude of compounds present in petrochemical wastes results in a variety of adverse effects that may be exerted on the environment. A number of different methods have been used to classify these pollutional effects, and they are categorized as follows: (a) direct effects on the nature of the receiving waters, (b) effects on the usability of the water, and (c) physiological effects on the biological systems which either inhabit the receiving waters or use them for purposes which might render them subject to these effects. It should be recognized that groundwater as well as surface water supplies can be subject to petrochemical pollution. Although the effects of pollution on surface water are more readily apparent, the less obvious pollution of groundwater is equally important. The extent of some pollutional effects on surface waters is documented (Klein, 1962; Hynes, 1965; Phelps, 1944). Specific cases of pollution by petrochemicals in the Mississippi River have been cited (Middleton, Licntenberg, 1960;Palange, 1960) and in Europe (Krombach and Barthel, 1964).

EFFECTS OF POLLUTION ON RECEIVING WATERS

Many pollutional effects of wastes are interralated. For example, biological and physical changes within a body of water receiving wastes might affect the magnitude and diversity of the aquatic organisms present. Additionally, water use might be affected by the presence of an undesirable physical characteristic, such as color.

Aesthetic Effects

The most graphic evidence of pollution is an unsightly and odoriferous effluent caused by various types of pollutants. The most obvious odors in receiving waters are those which result from the anaerobic decomposition of organic materials (Kneese, 1962). Visible effects of pollution, such as floating material, colored or turbid water, and foaming are objectionable from an aesthetic standpoint. The growth of large crops of algae caused by the addition of plant nutrients in the form of nitrogen and phosphorus can cause unsightly conditions (Kneese, 1962). Rubber particles from synthetic rubber manufacture may be present in waste effluent from these plants and are insoluble, relatively non-biodegradable, and floatable.

exceed the rate of oxygen replenishment from atmospheric or photosynthetic sources and this oxygen deficit can result in an anaerobic environment which may cause deleterious effects. Anaerobic conditions will also kill or drive off any aerobic organisms present in the water, including fish and higher animals. Organic suspended solids may settle out on stream bottoms where they undergo slow anaerobic degradation. These settled organic solids can be resuspended during high stream flows and may exert an unexpected oxygen demand on the stream. The biochemical oxygen demand (BOD) values for many common petrochemicals are tabulated in Table VI-1.

Thermal pollution can have several biological effects on receiving waters. Increasing temperatures increase the rate of biological activity, enhance atmospheric oxygen transfer to the liquid phase, and decrease oxygen solubility in water. The net result of a temperature increase is the exertion of a higher oxygen demand on the system, causing possible anaerobic conditions which might not have occurred at normal temperatures. At temperatures exceeding 35°C, many aquatic microorganisms will not survive (Anon., API, Vol. III.,1958). There are, however, some resistant species of bacteria and algae which can tolerate temperatures as high as 55°C.

Most fish are adversely affected by elevated temperatures. Some of these unfavorable effects are listed below (Klein, 1962):

a) death of the fish due to temperature above the lethal limits;

b) death due to shock from a sudden temperature change;

c) death due to dissolved oxygen concentrations below the lethal limit, resulting from the decrease in oxygen solubility at increased temperatures;

d) decreased productivity at temperatures which are nonlethal, but which exceed optimum spawning and egg-hatching levels; and

e) increased toxicity of certain chemicals to fish at elevated temperatures.

The lethal temperatures for some of the more important game fish are listed in Table VI-2. Lethal effects of heated effluents are discussed in detail in the paper by Alabaster (1964). The temperatures given in Table VI-2 do not reflect the possibility that temperatures below these lethal maximums may disrupt the reproduction of the species in question. The effects of water temperature on the reproduction of various species of fish are still not fully understood; however, these effects are of vital importance when the disposal of a high temperature waste is considered.

In a survey downstream from a plant producing butadiene and copolymer rubbers, 650 pounds of rubber particles were found in a 25-mile stretch of river (Dougan and Bell, 1951). Oil is a common petrochemical pollutant which is lighter than water and will float. Oils can be present in wastewaters either as free oil or as emulsified oil. Generally, emulsified oils are dispersed throughout the wastewater and will not physically separate from the aqueous phase. Very small amounts of some oils can impart an iridescent sheen to a body of water. It has been calculated that as little as 25 gallons of oil distributed over a water surface of one square mile would be barely visible, but 200 gallons on the same area would cause bright, iridescent colors on the water surface (Anon., API, Vol. I., 1953).

Surface-active materials in petrochemical wastes, principally from detergent manufacture, can cause foaming in receiving waters. Some of these agents, particularly synthetic detergents such as alkyl benzene sulfonate, are not readily degraded biologically, and concentrations sufficient to cause foaming in receiving waters often pass through waste treatment plants unaltered. As little as 0.5 mg/l of alkyl benzene sulfonate can result in foaming. New synthetic detergents such as linear alkyl sulfonate and alpha olefin sulfonate are biodegradable and have contributed towards alleviation of the foaming problem. Most of the reported cases of foaming in surface waters are caused by municipal wastes, but the possibility of surface-active materials in wastes from petrochemical plants manufacturing detergents also must be considered. Equipment washing operations may also contribute surface-active agents to petrochemical waste streams and must be recognized as another possible source of these materials.

Many organic and inorganic compounds present in petrochemical effluents can impart color to receiving waters. Anaerobic decomposition can also cause a body of water to become black and unsightly. Color has been discussed more thoroughly in the section on the pollutional characteristics of petrochemical wastes.

Suspended solids can cause both color and turbidity. Turbidity is a very objectionable quality not only as far as a aesthetic aspects are concerned, but also because it decreases light penetration, thus inhibiting photosynthetic organisms.

Biological Effects

Petrochemical wastes can exert a multiplicity of biological effects in receiving waters. The most prominent effect of biodegradable organic matter is the biochemical oxygen demand which it exerts on the receiving bodies of water. Aerobic microbial action utilizes the dissolved oxygen in water to convert organic contaminants into new cellular products, partially oxidized intermediates, carbon dioxide, and water. When large quantities of organic matter are involved, the rate of oxygen demand by aerobic processes may exceed the rate of oxygen replenishment from atmospheric or photosynthetic sources and this oxygen deficit can result in an anaerobic environment which may cause deleterious effects. Anaerobic conditions will also kill or drive off any aerobic organisms present in the water, including fish and higher animals. Organic suspended solids may settle out on stream bottoms where they undergo slow anaerobic degradation. These settled organic solids can be resuspended during high stream flows and may exert an unexpected oxygen demand on the stream. The biochemical oxygen demand (BOD) values for many common petrochemicals are tabulated in Table VI-1.

Thermal pollution can have several biological effects on receiving waters. Increasing temperatures increase the rate of biological activity, enhance atmospheric oxygen transfer to the liquid phase, and decrease oxygen solubility in water. The net result of a temperature increase is the exertion of a higher oxygen demand on the system, causing possible anaerobic conditions which might not have occurred at normal temperatures. At temperatures exceeding 35°C, many aquatic microorganisms will not survive (Anon., API, Vol. III.,1958). There are, however, some resistant species of bacteria and algae which can tolerate temperatures as high as 55°C.

Most fish are adversely affected by elevated temperatures. Some of these unfavorable effects are listed below (Klein, 1962):

a) death of the fish due to temperature above the lethal limits;

b) death due to shock from a sudden temperature change;

c) death due to dissolved oxygen concentrations below the lethal limit, resulting from the decrease in oxygen solubility at increased temperatures;

d) decreased productivity at temperatures which are nonlethal, but which exceed optimum spawning and egg-hatching levels; and

e) increased toxicity of certain chemicals to fish at elevated temperatures.

The lethal temperatures for some of the more important game fish are listed in Table VI-2. Lethal effects of heated effluents are discussed in detail in the paper by Alabaster (1964). The temperatures given in Table VI-2 do not reflect the possibility that temperatures below these lethal maximums may disrupt the reproduction of the species in question. The effects of water temperature on the reproduction of various species of fish are still not fully understood; however, these effects are of vital importance when the disposal of a high temperature waste is considered.

TABLE VI-1

FIVE-DAY BOD VALUES FOR SOME PURE ORGANIC COMPOUNDS OFTEN FOUND IN PETROCHEMICAL WASTES

Compound	BOD (gm/gm)	Method	Seed**	COD* (gm/gm)	Ref
Acid Anhydrides					
Phthalic Anhydride	0.72-1.26	Std. dil.	Sewage		51
Maleic Anhydride	0.4-0.6	Warburg	Sewage		
Alcohols					
Methanol	0.76-1.12; 1.24	Warburg	Sewage	1.42	28, 51, 91
Ethanol	0.93-1.67; 1.46	Warburg	Sewage	2.0	51, 91
			Acclimated	"	51
n-Propanal	0.47-1.5	Warburg	Sewage		
i-Propanal	1.29-1.59	Warburg	Sewage		
n-Butanal	1.1-1.65	Warburg	Sewage		
Cyclohexanol	0.08	Warburg	Sewage		
Ethylene Glycol	0.16-0.68	Warburg	Sewage		
Pentaerythritol	-	-	-	1.23	28
Aldehydes and Ketones					
Formaldehyde	0.33-1.06	Std. dil.	Sewage	1.06	28, 51
Acetaldehyde	1.27	Std. dil.	Sewage		
Furfural	0.77	Std. dil.	Sewage		
Acetone	0.31-1.63; 1.19	Std. dil.	Sewage	1.63	51, 91
			Acclimated	"	
Methyl Ethyl Ketone	2.14	Std. dil.	Sewage		
Esters					
Ethyl Acetate	0.29-0.86	Std. dil.	Sewage		
Ethers Diethylether	n:1	Std. dil.	Sewage		

TABLE VI-1 (Continued)

FIVE-DAY BOD VALUES FOR SOME PURE ORGANIC COMPOUNDS OFTEN FOUND IN PETROCHEMICAL WASTES

Compound	BOD (gm/gm)	Method	Seed**	COD* (gm/gm)	Ref
Halogenated Hydrocarbons					
Ethylene Dichloride	0.002	Std. dil.	Sewage		
Ethylene Chlorohydrin	0.5	Std. dil.	Sewage		
Chloroform	0-0.008	Std. dil.	Sewage		
Monochlorobenzene	0.03	Std. dil.	Sewage		
Hydrocarbons					
Benzene	0	Std. dil.	Sewage		51
Xylene	0	Std. dil.	Sewage		
Toluene	0; 1.23	Std. dil.	Sewage	1.88	51, 91
			Acclimated	"	
Naphthalene	0	Std. dil.	Sewage	"	
Nitrogen-containing Organics					
Nitrobenzene	0	Std. dil.	Sewage		
Pyridine	0-1.47	Std. dil.	Sewage		
Ethanolamine	0.78	Std. dil.	Sewage		
Diethanolamine	0.10	Std. dil.	Sewage		
Aniline	1.49-2.26	Std. dil.	Sewage	2.4	
p-Toluidine	1.44-1.63	Std. dil.	Sewage		
o-Toluidine	0.24-1.43	Std. dil.	Sewage		
Acrylonitrile	0.72	Std. dil.	Acclimated		28
Acrylamide Monomer	0.97	Std. dil.	Acclimated		
Adiponitrile	-	-	-	1.9	74
Hexamethylene Imine	1.31	Std. dil.	Acclimated	2.17	74

TABLE VI-1 (Continued)

FIVE-DAY BOD VALUES FOR SOME PURE ORGANIC COMPOUNDS OFTEN FOUND IN PETROCHEMICAL WASTES

Compound	BOD (gm/gm)	Method	Seed**	COD* (gm/gm)	Ref
Organic Acids					
Formic Acid	0.02-0.27	Std. dil.	Sewage		51, 91
Acetic Acid	0.34-0.88; 0.62	Std. dil.	Sewage	1.0	
			Acclimated	"	
Propionic Acid	0.36-0.84; 0.96	Std. dil.	Sewage	1.4	51, 91
			Acclimated	"	
Butyric Acid	0.34-0.90; 1.16	Std. dil..	Sewage	1.65	
			Acclimated	"	
Maleic Acid	0.38; 0.63	Warburg; Std. dil.	Sewage	0.93	51, 91
			Acclimated	"	
Benzoic Acid	1.34-1.40; 1.36	Std. dil.	Sewage	1.88	
			Acclimated	"	
Phthalic Acid	0.85-1.44; 1.4	Std. dil.	Sewage	0.86	
			Acclimated	"	
Methacrylic Acid	0.89	Std. dil.	Sewage		
Salycylic Acid	0.97	Std. dil.	Acclimated	1.58	51
Glutaric Acid	0.72	Std. dil.	Acclimated	1.21	74
Succinic Acid	0.57	Std. dil.	Acclimated	1.85	74
Valeric Acid	-	-	-	1.85	74

TABLE VI-1 (Continued)

FIVE-DAY BOD VALUES FOR SOME PURE ORGANIC COMPOUNDS
OFTEN FOUND IN PETROCHEMICAL WASTES

Compound	BOD (gm/gm)	Method	Seed**	COD* (gm/gm)	Ref
Phenolic Compounds					
Phenol	2.0	Manometric	Adapted	3.2	51
Phenol	1.4-1.8; 1.66	Std. dil.	Sewage	2.28	51 , 91
			Acclimated	"	
o-Cresol	1.69; 1.74	Std. dil.	Sewage	2.39	91
			Acclimated	"	
m-Cresol	1.70; 1.88	Std. dil.	Sewage	2.4	
			Acclimated	"	
p-Cresol	1.4; 1.76	Std. dil.	Sewage	2.4	
			Acclimated	"	51
1, 3, 5-Xylenol	0.82	Std. dil.	Sewage		

---

* By Dichromate Method - Standard Methods, 1965

** BOD values obtained by the use of sewage seed (unacclimated waste seed) may not be representative and most likely are low.

TABLE VI-2

LETHAL TEMPERATURES FOR SOME SELECTED FISH SPECIES

(Reference 59)

Fish	Lethal Temperature* (^oC)
Bluegill	30.7
Brown Trout	23-26
Carp	31-34
Catfish	31.8
Chinook Salmon (fry)	25
Coho Salmon	24.3
Fathead Minnow	28.2-33.2
Goldfish	30.8
Largemouth Bass	32.5-36.4
Perch	23-25
Rainbow Trout	28-24
Speckled Trout	25

---

[*] The lethal temperature is a function of the acclimation temperature of the test specimen. Higher acclimation temperatures will result in higher lethal temperatures.

The net biological effect of petrochemical waste pollution is a change in the environmental conditions in the receiving waters. Changes which are highly visible may occur, such as anaerobic conditions. Other changes may be more subtle in nature, and although not readily noticeable will possibly have far-reaching effects. Some of these subtle effects follow.

a) There are changes in the flora and fauna (bacteria, algae, protozoa) which are important elements in the food chain. Polluted water often favors the growth of one species of organism over others, and the degree of species diversity in natural waters has been used as a pollution indicator. The bloom of various algal species in water containing excess nitrates and phosphates is a well-known indicator. The change in predominance of one member of the food chain affects all the other members. For example, fish may have to leave an area if a lower-chain food organism is eliminated.

b) Pollutional effects may not injure the organisms present in the water but may alter their reproductive patterns so as to affect their progeny.

c) Various types of pollutants may affect the living habits of aquatic organisms and may cause an erratic pattern in their behavior.

Detailed accounts of the biological effects of pollution are available elsewhere (Klein, 1962; Tarzwell, et. al.,1965; Phelps, 1944; Anon., Oxygen Relationships in Streams, 1958).

Miscellaneous Effects

The effects of petrochemical wastes on the recreational capacity of receiving waters are closely related to the aesthetic and biological effects of wastes. Any pollution which causes unsightly conditions and kills or drives off sport fish will decrease the recreational aspects of the water.

Land use and transportation can also be affected directly by pollution since chemical pollutants may make water unsuitable for domestic, industrial, and agricultural uses. It is well known that land used for public domain, such as parks and recreational areas, depends upon the use of nearby bodies of water. Additionally, the discharge of wastes carrying large quantities of suspended or dissolved solids which precipitate under given conditions can result in the formation of sludge banks in the receiving water, thus affecting water-borne transportation (Anon., API, Vol. III.,1958). Waters of low pH can also corrode the steel hulls of ships.

EFFECTS OF POLLUTION ON WATER USE AND REUSE

Various petrochemical pollutants, both chemical and physical, may affect the potential future uses of wastewater or receiving waters.

Water Quality for In-Plant Reuse

In-plant reuse of wastewater by the petrochemical industry offers an economical approach for reducing wastewater discharges to receiving waters. Water quality required for various in-plant uses varies greatly with some processes requiring demineralized water, while cooling water can often contain considerable quantities of inorganic solids. The quality of water required for various petrochemical processes is discussed below.

Cooling Water

Recirculation of cooling water is now common practice in many petrochemical plants. The most important consideration in cooling water use is preventing the deposition of precipitates in water pipes and in the process coolers (Beychok, 1967). The solubilities of the most common salts found in cooling water are given in Table VI-3. The principal problems are caused by calcium carbonate, magnesium carbonate, and calcium sulfate as indicated by their low solubility. Water can be used for cooling purposes without pretreatment if the concentrations of these compounds, particularly the carbonates, are below the values in Table VI-3. It may be economically feasible to treat particular waste streams in order to render them suitable for cooling water reuse. Water used for cooling purposes should also be free of biological growth and should be noncorrosive. The latter requirement eliminates the use of acidic wastes as cooling water unless they are properly neutralized. Cooling water should have a low organic content because these materials serve as a substrate source and may create excessive biological growth. Potentially toxic metal and organic compounds are often added to prevent the growth of bacteria and algae and inhibit corrosion in cooling water (chromates, phosphates and polyphosphates, lignins and tannins, chlorinated phenols, copper compounds). The concentrations of these additives are usually sufficiently low to avoid toxicity problems.

Process Waters

Chemical processes used in the petrochemical industry require many levels of water quality. All of these processes with their respective quality requirements cannot be listed easily. Many processes have stringent prerequisites for their water and the required quality indicates the economic necessity for reusing some waste streams as process waters.

TABLE VI-3

SOLUBILITY OF COMMON SALTS*

	Chlorides	Carbonates	Sulfates
Calcium	520,000	17	2,200
Magnesium	270,000	125	330,000
Sodium	270,000	290,000	310,000

* At 120° F

Note: Solubilities are in mg/l.

Water Quality Required for Other Users

The effects of petrochemical wastes on the utility of water for other users is important. These other users can be grouped into three categories: domestic water supply, agricultural water supply, and industrial water supply. It should be mentioned that many "natural" waters, untouched by man-made pollution, do not meet the quality standards required by potential users without pretreatment. The pollution of water by petrochemical wastes is only an important factor when undesirable compounds which cannot be removed at all or which can only be removed at a high cost to the user are added to the water. Some of the petrochemical contaminants previously discussed fall into this category.

Agricultural Uses - Some of the compounds present in petrochemical wastes may be toxic to plants and livestock. High concentrations of inorganic dissolved solids are detrimental to both plants and livestock. Water given to livestock is nearly always untreated and must not contain toxic materials such as the catalytic heavy metals discharged from petrochemical processing. The water quality requirements for irrigation purposes are given in Table VI-4.

Since crops vary greatly in their sensitivity to salinity, the water qualities expressed in Table VI-4 are classified in terms of their relative suitability for irrigation purposes. It should be recognized that a few crops may be able to stand salinity concentrations in excess of these concentrations. Sodium, an important constituent of petrochemical spent caustic effluents, reacts with soil to reduce its permeability and thus is an important parameter for judging the utility of a water for irrigation (Todd, 1959).

Industrial Use - Industrial quality requirements are highly variable. Some industries such as brewing and distilling industries require high quality water. Others such as the chemical industry and those which use large quantities of cooling water can tolerate water relatively poor in quality. A recent nationwide survey of industries showed that 58 percent of those reporting treated all or part of their water intake (Anon., Water in Ind.,1965).

One industry which may be severely affected by petrochemical pollution is the fishing industry. Besides the possibility of fish mortality due to pollution, some petrochemicals have been blamed for the tainting of fish flesh.

Effects on Water Treatment Processes

Some compounds present in petrochemical wastes have been implicated in creating problems associated with conventional water

TABLE VI-4

WATER QUALITY FOR SELECTED AGRICULTURAL USES

(Reference 86)

Water Class	Percent Sodium of Cationic Content	EC X 10^6 at 25^oC	Boron, ppm			Total Solids (mg/1)
			Sensitive Crops	Semi-tolerant Crops	Tolerant Crops	
Excellent	< 20	< 250	<0.33	<0.67	<1.00	< 390
Good	20-40	250-750	0.33-0.67	0.67-1.33	1.00-2.00	390-1,200
Permissible	40-60	750-2,000	0.67-1.00	1.33-2.00	2.00-3.00	1,200-3,100
Doubtful	60-80	2,000-3,000	1.00-1.25	2.00-2.50	3.00-3.75	3,100-4,700
Unsuitable	>80	>3,000	>1.25	>2.50	>3.75	>4,700

treatment. Oils will interfere with coagulation and filtration processes (Gloyna and Malina, 1962) while organic acids have been suspected of causing deterioration of anionic exchange resins used for dimeralization (Skold and Wilkes, 1955).* Suspended solids may cause clogging and stoppage in the piping systems carrying them.

Surface-active chemicals, principally detergents, have caused foaming problems in some water treatment plants and can also impart tastes to drinking water.

Effects on Groundwater

During the three-year period from 1957 through 1959, 22 states reported groundwater pollution by oil or petroleum products and 15 states reported cases of pollution involving various other chemical contaminants (Anon., Comm. Rept., Task Grp. 245.,1960). Petrochemicals were specifically indicated as a source of groundwater pollution in one case, while high nitrate concentrations in well water were attributed to the lagooning of wastes from nitrogeneous fertilizer manufacture in another (Anon., Comm. Rept. Task Grp. 245., 1960). Disposal wells, lagoons, and surface dumping were the most important potential sources of pollution by petrochemical wastes listed in the report. Some of the organic compounds which have been found in groundwater are listed in Table VI-5 (Gloyna and Malina, 1962).

It is also possible for several innocuous compounds to react, forming a product which is far more toxic or creates a considerably more difficult taste and odor problem than the original compounds.

PHYSIOLOGICAL EFFECTS OF PETROCHEMICAL WASTES

Almost every effect of pollution can be considered a physiological effect in a general sense. The biological effects of organic wastes in receiving waters are in reality physiological effects on the inhabitants of the water. Even aesthetic effects can be considered physiological in that they act on the senses of man to produce a reaction. The physiological effects which will be considered here are those which are most prevalent to the observer, namely, taste, odor, and toxicity.

---

[*] Organic matter can also interfere with ion exchange processes by coating the resin or by reacting chemically with it (Bacon and Lewis, 1960). The annual losses which can be caused by organic interferences can be as high as 25 to 33 percent for anionic resins.

TABLE VI-5

ORGANIC CHEMICAL POLLUTANTS IDENTIFIED IN GROUNDWATER

(Reference 45)

Alkyl Benzene Sulfonates

2, 4-Dichlorophenoxyl Acetic Acid

Dichlorophenol

Gasoline

Hexachlorocyclohexane

Hydrocarbons

Nitrates

Oil

Pentachlorophenol

Phenol

Phosphates

Picoline

Picric Acid

Pyridine

Trichloroethylene

It is first important to understand the effects which mixtures of compounds have on the toxicity or taste and odor of the individual components. Antagonism occurs when the mixing of two or more compounds causes the effects of each to be reduced. The combined effects are therefore less than the sum of the individual effects. Synergism is the cooperative action of each component in a mixture, so that the effect produced by the mixture is equal to or greater than the sum of the effects considered independently. Recently, a new term - potentiation - has been used to describe the latter effect while synergism has been used to describe the former. However, the term synergism is commonly used to describe both effects.

Most investigations concerning taste and odor have not included these effects due to the difficulty in assessing them. More research is required to identify these synergistic and antagonistic interactions and until this is accomplished only general statements about the effects can be made.

Taste and Odor

The senses of taste and odor are virtually inseparable in most cases and most investigations emphasize or deal exclusively with odor, since taste effects are biased by olfactory sensations. (Baker, 1963). Probably the best discussion of these physiological properties and all their implications is given in a review by Baker prepared for the Manufacturing Chemist's Association (1961). Detailed discussions of the various theories pertaining to taste and odor are given in this review and in others (Haines, et. al., 1954; Anon., Soc. of Chem. Ind., 1957; Timmermans, 1954; Wright, et. al., 1956).

Many compounds in petrochemical wastes cause tastes and odors at very low concentrations with the synergistic effects of complex mixtures significantly magnifying these effects. A study utilizing the chemicals, m-cresol, n-butanol, pyridine, n-butyl-mercaptan, n-amyl acetate, acrylonitrile, 2-4 dichlorophenol, and acetophenone showed marked synergistic effects. A mixture containing each compound at its threshold value produced a significant olfactory response (Baker, 1963). Binary mixtures of selected pairs of these compounds showed similar effects. Any or all of these chemicals might be found in a petrochemical effluent, and the significance of these results in taste and odor problems is apparent.

Detectable concentrations of some common petrochemical waste constituents are listed in Table VI-6. Probably the most common and most objectionable odor-causing compound contained in this list is hydrogen sulfide. Hydrogen sulfide may be present in petrochemical wastes or may be formed during the anaerobic decomposition of these wastes.

TABLE VI-6

DETECTABLE CONCENTRATIONS OF SOME PETROCHEMICAL COMPOUNDS CAUSING TASTE AND ODOR IN WATER

Compound	Detectable Concentration (mg/l)	Reference
Ammonia	0.037	59
Amyl Acetate (iso)	0.0006	59
Benzaldehyde	0.003	59
Carbon Disulfide	0.0026	59
Chlorophenolics	0.001 - 0.1	11
- Monochlorophenol	0.00018	59
Dimethylamine	0.6	81
Ethyl Mercaptan	0.00019	11
Formaldehyde	50.0	11
Furfural	4.0	11
Hydrogen Cyanide	0.001	51
Hydrogen Sulfide	0.001	59
Methyl Mercaptan	0.0011	59
Nitrobenzene	0.03	59
Petrochemical Wastes	0.015 - 0.1	59
Phenolics	0.25 - 4.0	11
Phenyl Ether	0.013	11
Picolines	0.5 - 1.0	11
Refinery Hydrocarbons	0.025 - 0.05	11
Sulfur Dioxide	0.009	59
Xylenes	0.3 - 1.0	11

Compounds containing nitrogen, principally the amines, are also malodorous and are found in various petrochemical wastes, particularly in those discharged from synthetic fiber manufacture (Taylor, et. al.,1961).

Phenol probably has been the organic chemical most often associated with taste and odor problems. The United States Public Health Service Standards establishing maximum allowable phenol concentrations in drinking water are based solely upon taste and odor considerations. Phenol itself is relatively odorless and tasteless, the minimum detectable concentration being 0.25-4.0 mg/l (Baker, 1963). The taste and odor problems caused by phenols occur when water is disinfected by chlorination. Dichlorophenols are formed and give water a characteristic medicinal taste at concentrations as low as one ppb. Various studies have shown the mechanisms by which chlorophenols are formed and the conditions required for their formation (Burttschell, et. al.,1959). Recent investigations have shown that taste and odor problems cannot always be correlated with phenol concentrations, indicating that other organic compounds are often responsible for these conditions (Kinney, 1960a; Kinney, 1960b). For example, other chlorinated hydrocarbons have been identified as a major source of tastes and odors.

Petrochemical wastes contain many organic chemicals which can interact to produce tastes and odors. A study of a refinery wastewater indicated that the neutral organic compounds (nonpolar) consisting principally of aliphatic and aromatic hydrocarbons were the primary source of odor in the wastewater (Ruchhoft, et. al., 1954). The oxygenated and aromatic fractions of the neutral organic groups were also found to be the most odiferous in a similar investigation. This was found to be a complex mixture of hydrocarbons, alcohols, aldehydes, ketones, esters, and nitriles; and the odors caused by this fraction could not be attributed to any single compound (Middleton, et. al.,1956). Many neutral organic compounds are commonly found in petrochemical wastes. Organic acids are also found, and many of these acids can cause tastes and odors in water. Alkyl benzene sulfonates can be detected by some people at concentrations below one mg/l (Klein, 1962; Filicky and Hassler, 1950). Many taste- and odor-producing compounds are therefore potentially present in petrochemical wastewaters. Since tastes and odors in water have such an anverse effect on many uses, each waste must be carefully tested to determine if it causes such an effect and if so, what treatment must be required.

One instance in which taste can be separated from odor is in the causation of adverse tastes in fish flesh. Some organic chemicals can cause the flesh of fish to become "tainted," rendering the fish useless as a food source. A few chemicals which may be found in petrochemical effluents and are able to cause these effects are listed in Table VI-7. Styrene and aldehydes from synthetic rubber manufacture have also been demonstrated to taint fish flesh (Klein, 1962).

Many natural compounds can also produce tastes and odors in water. Decaying vegetation is often responsible for releasing phenolic compounds to water (Hoak, 1956; Smith, 1961) and hydrogen sulfide, mercaptans, and organic nitrogen compounds are formed during the anaerobic decomposition of organic material. Algae and their metabolic products are probably the most important cause of taste and odor while other microorganisms such as actinomycetes have also been implicated (Baker, 1961; Silvey, et. al.,1950).

Toxicity

Toxicity includes the effects of pH, lack of dissolved oxygen, high temperature, and high dissolved solids as well as compounds which are classified as poisons. It is the poison effect which will be considered.

The toxicity of a chemical is directly related to the dosage of the chemical ingested or otherwise taken into the body of the aquatic organism. In water the toxic effects of a chemical can best be described in terms of the concentration threshold, above which some type of physiological damage to the organism will not affect the subject during its normal life span, even if the compound is administered throughout the life span. This later effect has been demonstrated for every toxic compound which has been studied, including the chemical carcinogens (Zapp, 1960).

It is desirable to distinguish between the classes of toxic action. These classifications are established on the basis of the rate of action of the toxicant, the duration of the symptoms, and the rate of intake of the compound (Gloyna and Malina, 1962).

Acute toxicity is characterized by the rapid onset of negative physiological effects after exposure. Chronic toxicity is usually manifested by the appearance of negative physiological effects after a prolonged dosage of a chemical at concentrations below the acute level. These effects are often the result of the accumulation of the toxic compound in the tissues or organs of the organism. The mode of action of toxic compounds depends on their chemical characteristics and is discussed in detail in many books on toxicology, (i.e., Dubois and Geiling, 1959).

While the toxic effect of petrochemicals on man is of great interest, concentrations of these chemicals in water is usually so low that their principal toxic effects on man are generally chronic. Carcinogenesis is the chronic effect which has probably received the most attention. Many compounds which have been found to exhibit carcinogenic effects are present in petrochemical wastes of which

TABLE VI-7

SOME ORGANIC CHEMICALS CAUSING ADVERSE TASTES IN FISH

Compound	Type Fish Tested	Approx. Concen. Causing Taste (mg/1)	Ref
Phenol	Trout, Carp	25*; 1.0	59, 82
Cresols	Trout, Carp	10	59
1, 3, 4-Xylenol	Carp	5	59
1, 3, 5-Xylenol	Rudd	1	59
1, 2, 4-Xylenol	Rudd	1	59
Pyrocatechol	Carp	2.5	59
Resorcinol	Carp	30.0	59
p-Toluidine	Rudd	20.0	59
Pyridine	Carp, Rudd	5.0	59
Quinoline	Carp	0.5-1.0	59
Naphthalene	Rudd	1.0	59
α -Naphthylamine	Rudd	3.0	59
o-sec butyl Phenol	Not Reported	0.3	82
p-tert butyl Phenol	Not Reported	0.03	82
o-Phenylphenol	Not Reported	1.0	82
o-Chlorophenol	Not Reported	0.015	82
p-Chlorophenol	Not Reported	0.05	82
2,4-Dichlorophenol	Not Reported	0.005	82
Diphenyloxide	Not Reported	0.05	82
Acetophenone	Not Reported	0.5	82
Styrene	Not Reported	0.25	82
α -Methylstyrene	Not Reported	0.25	82
Isopropylbenzene	Not Reported	0.25	82
Ethyl Benzene	Not Reported	0.25	82
ββ -Dichloroethylether	Not Reported	1.0	82
o-Dichlorobenzene	Not Reported	<0.25	82
Toluene	Not Reported	<0.25	82
Cresylic Acid (m,p)	Not Reported	0.2	82
Kerosene	Not Reported	0.1	82

* Above Toxic Limit

** Test Fish Not Reported

certain polynuclear aromatic compounds, aromatic amines, and aromatic nitro-compounds are examples. The complex hydrocarbons and tars have also been indicated as possible carcinogenic agents (Hueper, 1960). These compounds can originate from any petrochemical processes, and many of them are probably present in petrochemical wastewaters. However, the concentrations of these compounds in receiving waters are generally low. Little is known about the physiological effects of chronic exposure to these compounds and the possibility of synergistic action between a number of these compounds. The use of carbon chloroform extract from water samples has been proposed as a basis for limiting the exposure of man to these compounds (Ettinger, 1960). The most recent United States Public Health Service drinking water standards (1962) recommend an arbitrary maximum carbon chloroform extract concentration of 0.2 mg/l. Much more data are needed before the actual chronic effects of these compounds on man can be accurately determined.

The toxicity of other chemicals which have petrochemical origins has also been investigated, but most of these studies deal with gaseous contaminants such as nitrogen dioxide (Cooper and Tabershaw, 1966). Few studies have been made which show the effects on higher animals by the ingestion of organic chemicals via the water route. Some research has been directed toward determining the toxicity effects of surface-active materials in water indicating that these compounds do not have chronic effects on higher animals at concentrations up to 1,000 mg/l in drinking water (Paynter, 1960).

A great deal of data is available on the toxicity of chemical compounds to aquatic organisms. The toxicity of many petrochemical pollutants has been evaluated using both microorganisms and fish. It must be noted that most of these investigations determine the acute toxicity of a compound to a particular organism. Chronic effects and any effects on the genetic reproduction characteristics of the organism are difficult to determine and not usually listed. Therefore, the toxicity data which are presented can only represent the relative toxicity of a compound and do not consider the effects of other toxic compounds which might be present.

Toxicity to Microorganisms - Toxic effects of chemicals on aquatic microorganisms are extremely important. Bacteria in natural waters decompose the organic material from petrochemical wastes and subsequently serve as the food source for some higher microorganisms such as protozoa. Protozoa and algae both serve as food sources for macro-organisms (insects, fish) and algae are extremely important in that they contribute an important source of oxygen to the receiving waters via photosynthesis. The extinction of any of these organisms due to toxic chemicals will have a profound adverse effect on the general ecology of the aquatic system.

Two detailed investigations of the toxicity of certain organic chemicals to algae have recently been reported. (Thirumurthi and Gloyna, 1965; Huang and Gloyna, 1967). The results of these studies are applicable to petrochemical wastes contaminants and are shown in Table VI-8. The algae used in these investigations was Chlorella pyrenoidosa, a common inhabitant of ponds and streams. Toxicity was determined by measuring the reduction in chlorophyll content of a suspension of algae exposed to the compound under rigidly controlled environmental conditions. Reduction in oxygen production as measured manometrically was also used as an indication of chemical toxicity (Huang and Gloyna, 1967). The effects of environmental conditions on toxicity cannot be overemphasized. Slight changes in temperature, incident light, and nutrients significantly affect the nature of a compound as a toxicant.

Data obtained using structurally similar fatty acids, alcohols, and aldehydes indicate that relative toxicity is somewhat dependent upon the molecular structure. These data suggest that (a) straight-chain fatty acids with an odd number of carbon atoms are more toxic than those with an even number of carbon atoms, and (b) the straight-chain fatty acids with four- and five-carbon atoms are more toxic than the corresponding branched-chain acids. In general, straight-chain organics seem to be more toxic than those with branched-carbon chains (Thirumurthi and Gloyna, 1965).

It has been observed that certain phenolic compounds and pesticides reduce the chlorophyll concentration and photosynthetic activity of Chlorella pyrendoisa (Huang and Gloyna, 1967). The toxicity of phenolic compounds to this algae was found to be dependent on the functional groups attached to the ring and their position on the ring. Nitrated and halogenated phenols are more toxic than alkylated and aminated phenols. The insecticide Lindane was found to be about 100 times as toxic to Chlorella pyrenoidosa as was phenol (Huang and Gloyna, 1967).

These investigations reveal that many compounds commonly found in petrochemical effluents are highly toxic to algae. The effects of this toxicity on the oxygen resources of a receiving body of water or waste stabilization pond treatment system must be considered when the toxic properties of a waste are being evaluated.

The use of microorganisms such as algae for indicators of toxic pollutants will be discussed subsequently.

Fish Toxicity - Fish are the test animals most frequently used in determining the toxicity of aqueous wastes. This is true for two reasons: (a) they are relatively easy to use and control, and (b) their response to toxic materials is one of the more valid indicators of the true toxicity in natural waters. The toxicity

TABLE VI-8

TOXICITY OF SOME SELECTED PETROCHEMICALS TO CHLORELLA PYRENOIDOSA

Organic Chemical	Toxic Conc. (mg/l)*	Ref
Alcohols		
Methanol	31,100	84
Ethanol	27,200	84
1 - propanal	11,200	84
2 - propanal	17,400	84
1 - butanal	8,500	84
2 - butanal	8,900	84
3 - butanal	24,200	84
Aldehydes		
Propanal	3,450	84
1 - butanal	2,500	84
Glycols		
1, 2 Ethanedial (Ethylene glycol)	180,000	84
1, 2 Propanediol	92,000	84
Pesticides		
Lindane	2.3	50
2, 4 - D	144	50
2, 4, 5 - T	122	50
DDT in Xylene	120.0	84
Malthane	160.0	84
Phenolics		
Phenol	1,060	84
Phenol	233	50
Cresol	800	84
Cresols (ortho,meta, para)	148 - 171	50
o-Bromophenol	78	50
m,p-Bromophenol	36	50
o-Chlorophenol	96	50
m,p-Chlorophenol	40	50
2, 4 - Dichlorophenol	21	50
2, 4, 5 - Trichlorophenol	1.5	50
Pentachlorophenol	0.001	50
Xylenols	49 - 81	50

TABLE VI-8 (Continued)

TOXICITY OF SOME SELECTED PETROCHEMICALS TO CHLORELLA PYRENOIDOSA

Organic Chemical	Toxic Conc. (mg/1)*	Ref
Nitrophenols	9 - 14	50
o-Aminophenol	47	50
m,p-Aminophenols	140	50
Hydroquinone	178	50
Organic Acids and Salts		
Methanoic acid	220	84
Ethanoic acid	350	84
Propanoic acid	250	84
Butanoic acid	340	84
2-Methyl Propanoic acid	345	84
Pentanoic acid	280	84
Propenoic acid	120	84
Butenoic acid	280	84
Ethanoic anhydride	360	84

* Based on 50% Reduction in Chlorophyll Content

of a chemical is a function of the prevailing environmental conditions. The most important environmental parameters in toxicity tests include pH, temperature, dissolved oxygen concentration, and the water hardness (Cairns, 1957). These environmental factors are controlled in the laboratory bioassay which is the most commonly used method for defining the acute toxicity of a specific compound to fish. The bioassay basically consists of exposing acclimated fish to various concentrations of the test compound. These procedures are completely described in other sources (Jones, 1964; Standard Methods, 1965).

The most commonly accepted fish toxicity parameter is the median tolerance limit (TL_M) which is the concentration of the test compound at which 50 percent of the test fish survive for a selected test period. The TL_M values obtained from the bioassay are a measure of the acute toxicity of a specific chemical and cannot be used to estimate possible chronic or cumulative effects. In cases where it is necessary to measure the toxicity of a mixed chemical waste, a bioassay using various concentrations of the mixed waste is used to determine the toxic concentration. The TL_M values for an industrial waste of complex composition are reported as a percent by volume dilution (Standard Methods, 1965). For example, a 10 percent TL_M represents one part of wastewater diluted with nine parts of receiving water.

A great deal of bioassay data are available for a variety of chemicals and species of fish. The TL_M values for many of the compounds found in petrochemical wastes are given in Table VI-9. Included with the TL_M values for pure compounds are some TL_M values for mixed wastes. By measuring the toxicity of a mixed waste, the possibility of a reaction of nontoxic compounds in the waste to form toxic compounds is considered. For example, a cholinesterase-inhibiting compound was found naturally in the effluent formed in a chemical plant by the oxidation of its precursor, which was manufactured in the plant (Teasley, 1967). Synergistic and antagonistic effects can also be taken into account by using this procedure. It can be seen from Table VI-9 that the toxic concentrations for a given compound are dependent upon the species of fish tested and the hardness of the test water. These factors must be considered when the toxic effects of a pure compound are applied to a natural stream. In general, game fish such as trout and bass are more sensitive to the toxic effects of chemicals than are forage and "rough" fish.

Median tolerance limits (TL_M) determined in the laboratory can be used only to estimate the toxicity of a compound to a given species of fish under the environmental conditions imposed in the laboratory. Since "no effect" or less than threshold concentrations

TABLE VI-9

TOXICITY BIOASSAY RESULTS

Compound	TL_m (Median Tolerance Limit) 24 Hr (mg/l)	48 Hr (mg/l)	96 Hr (mg/l)	Test Animal	Remarks	Ref
Acetamide	26,300	26,300	13,300	Mosquito fish		88
Acetic Acid	251	251	251	Mosquito fish		88
Acetone	13,500	13,000	13,000	Mosquito fish		88
Acetaldehyde	70			Pinperch		
Acetonitrile			1,020	Fathead Minnows	Hard Water	47
			1,000	Fathead Minnows	Soft Water	47
			1,850	Bluegill	Soft Water	47
			1,650	Guppies	Soft Water	47
Acrylonitrile			14.3	Fathead Minnows	Hard Water	47
			18.1	Fathead Minnows	Soft Water	47
			11.8	Bluegill	Soft Water	47
			33.5	Guppies	Soft Water	47
			24.5	Pinperch		42
Adiponitrile			820	Fathead Minnows	Hard Water	47
			1,250	Fathead Minnows	Soft Water	47
			720	Bluegill	Soft Water	47
			775	Guppies	Soft Water	47
Alkyl Aryl Sulfonate	4.2	3.7	0.86	Bluegill		87
4-Amino-m-Toluene Sulfonic Acid	425	410	375	Mosquito fish		88
Ammonia			8.2	Fathead Minnows	Hard Water	47
Ammonium Acetate	238	238	238	Mosquito-fish		88
n-Amyl Acetate	65	65	65	Mosquito fish		88

TABLE VI-9 (Continued)

TOXICITY BIOASSAY RESULTS

Compound	TL_m (Median Tolerance Limit) 24 Hr (mg/1)	48 Hr (mg/1)	96 Hr (mg/1)	Test Animal	Remarks	Ref
Benzonitrile			78	Fathead Minnows	Hard Water	47
			135	Fathead Minnows	Soft Water	47
			78	Bluegill	Soft Water	47
			400	Guppies	Soft Water	47
Benzene	395	395	386	Mosquito fish		88
	20	20	6	Bluegill		87
Benzoic Acid	240	225	180	Mosquito fish		88
Butadiene	71.5			Pinperch		42
2-Butanone	5,600	5,600	5,600	Mosquito fish		88
Carbon Disulfide	162	135	135	Mosquito fish		88
o-Chlorophenol	8.2	8.1		Bluegill		62
Cresol	24	24	24	Mosquito fish		88
			13.6	Bluegill	Small (3.88 cm)	23
			10.9	Bluegill	Medium (6.09cm)	23
			10.0	Bluegill	Large (14.24cm)	23
Cupric Chrome - Gluconate	420	365	83	Bluegill		87
1-Cyano-1, 3 Butadiene	71.5			Pinperch		42
DDT (25% active in xylene)			0.180	Acroneuria Pacifica		43
			0.100	Pteronarcys California		43
			0.010	Claassenia sabulosa		43
			0.001	Daphnia magna		43
			0.100	Arctopsyche grandis		88
Diethanolamine	1,800	1,550	1,400	Mosquito fish		88
	2,100	1,850	430	Bluegill		87

TABLE VI-9 (Continued)

TOXICITY BIOASSAY RESULTS

Compound	TL_m (Median Tolerance Limit) 24 Hr (mg/1)	48 Hr (mg/1)	96 Hr (mg/1)	Test Animal	Remarks	Ref
Diethylene Glycol	32,000	32,000	32,000	Mosquito fish		88
Furfural	44	44	24	Mosquito fish		88
	32	16	1.2	Bluegill		87
Heptane	4,924	4,924	4,924	Mosquito fish		88
Hydrogen Cyanide	0.069			Pinperch		42
Lactonitrile	0.215			Pinperch		42
			0.90	Fathead Minnows	Hard Water	47
			0.90	Fathead Minnows	Soft Water	47
		4.009	0.90	Bluegill	Soft Water	47
			1.37	Guppies	Soft Water	47
Malathion (59% active xylene)		0.0009		Daphnia magna		
			0.0056	Acroneuria Pacifica		43
			0.100	Pteronarcys California		43
			0.056	Claassenia sabulosa		43
			0.032	Arctopsyche grandis		43
Maleic Anhydride	240	240	230	Mosquito fish		88
Methyl Ethyl Ketone	5,640	5,640	1,690	Bluegill		87
Napthalene	220	165	150	Mosquito fish		88
Oxydipropionitrile			3,920	Fathead Minnows		47
			3,600	Fathead Minnows		47
			4,200	Bluegill		47
			4,450	Guppies		47
o-Nitrophenol	66.9	46.3- 51.6		Bluegill		62

TABLE VI-9 (Continued)

TOXICITY BIOASSAY RESULTS

Compound	TL_m (Median Tolerance Limit) 24 Hr (mg/1)	48 Hr (mg/1)	96 Hr (mg/1)	Test Animal	Remarks	Ref
Parathion (25% active in xylene)			0.0001	Acroneuria Pacifica		43
			0.0032	Pteronarcys Californica		43
				Claassenia sabulosa		43
Phenol	61	56	0.001	Arctopsyche grandis		43
	22.7	22.2	56	Mosquito fish		88
				Bluegill		62
			13.5	Bluegill	Small (3.88cm)	23
			20.0	Bluegill	Medium (6.09cm)	23
			11.5	Bluegill	Large (14.24cm)	23
	19	19	5.7	Bluegill		87
Pyridine	1,350	1,350	1,350	Mosquito fish		88
Pyridyl Mercuric Acetate	12.5	11.3	2.8	Bluegill		87
Sodium Butyl Mercaptide	7.4	5.5	0.92	Bluegill		87
Sodium Cyanide			0.35	Fathead Minnows	Hard Water	47
			0.23	Fathead Minnows	Soft Water	47
			0.15	Bluegills	Soft Water	47
Sodium Oxalate	1,350	1,350	1,350	Mosquito fish		88
Tetraethyl lead	2.0	1.4	0.20	Bluegill		87
Toluene	1,340	1,260	1,180	Mosquito fish		88
Benzene (reagent)	35.56	35.08	33.47	Fatheads	Soft Water	73
	34.42	32.00	32.00	Fatheads	Hard Water	73
	22.49	22.49	22.49	Bluegill	Soft Water	73
	34.42	34.42	34.42	Goldfish	Soft Water	73
	36.60	36.60	36.60	Guppies	Soft Water	73

TABLE VI-9 (Continued)

TOXICITY BIOASSAY RESULTS

Compound	TL_m (Median Tolerance Limit) 24 Hr (mg/1)	48 Hr (mg/1)	96 Hr (mg/1)	Test Animal	Remarks	Ref
Chlorobenzene	29.12	29.12	29.12	Fatheads	Soft Water	73
	33.93	33.93	33.93	Fatheads	Soft Water	73
	39.19	34.98	33.93	Fatheads	Hard Water	73
	24.00	24.00	24.00	Bluegill	Soft Water	73
	73.03	56.00	51.62	Goldfish	Soft Water	73
	45.53	45.53	45.53	Guppies	Soft Water	73
o-Chlorophenol	21.96	19.12	11.63	Fatheads	Soft Water	73
	21.52	18.00	14.48	Fatheads	Hard Water	73
	11.31	10.59	10.00	Bluegill	Soft Water	73
	14.48	12.37	12.37	Goldfish	Soft Water	73
	22.17	20.78	20.17	Guppies	Soft Water	73
3-Chloro-propene	24.00	24.00	19.78	Fatheads	Soft Water	73
	25.86	24.00	24.00	Fatheads	Hard Water	73
	59.30	42.33	42.33	Bluegill	Soft Water	73
	26.56	20.87	20.87	Goldfish	Soft Water	73
	57.68	53.54	51.08	Guppies	Soft Water	73
o-Cresol	Not found	Not found	12.55	Fatheads	Soft Water	73
	18.00	13.42	13.42	Fatheads	Hard Water	73
	22.17	20.78	20.78	Bluegill	Soft Water	73
	Not found	Not found	23.25	Goldfish	Soft Water	73
	49.13	25.31	18.85	Guppies	Soft Water	73
Cyclohexane	35.08	35.08	32.71	Fatheads	Soft Water	73
	42.33	42.33	42.33	Fatheads	Hard Water	73
	42.33	40.60	34.72	Bluegill	Soft Water	73
	42.33	42.33	42.33	Goldfish	Soft Water	73
	57.68	57.68	57.68	Guppies	Soft Water	73

TABLE VI-9 (Continued)

TOXICITY BIOASSAY RESULTS

Compound	TL_M (Median Tolerance Limit) 24 Hr (mg/1)	48 Hr (mg/1)	96 Hr (mg/1)	Test Animal	Remarks	Ref
Ethyl Benzene	48.51	48.51	48.51	Fatheads	Soft Water	73
	42. 33	42.33	42.33	Fatheads	Hard Water	73
	35.08	32.00	32.00	Bluegill	Soft Water	73
	94.44	94.44	94.44	Goldfish	Soft Water	73
	97.10	97.10	97.10	Guppies	Soft Water	73
Ioprene	86.51	86.51	86.51	Fatheads	Soft Water	73
	74.83	74.83	74.83	Fatheads	Hard Water	73
	42.54	42.54	42.54	Bluegill	Soft Water	73
	180.00	180.00	180.00	Goldfish	Soft Water	73
	240.00	240.00	240.00	Guppies	Soft Water	73
Methyl Methacrylate	421.2	338.2	159.1	Fatheads	Soft Water	73
	455.1	455.1	160.2	Fatheads	Soft Water	73
	498.6	338.2	311.0	Fatheads	Hard Water	73
	391.9	368.1	320.0	Fatheads	Hard Water	73
	368.1	357.5	232.2	Bluegill	Soft Water	73
	423.3	423.3	277.1	Goldfish	Soft Water	73
	368.1	368.1	368.1	Guppies	Soft Water	73
Phenol (U.S.P. 100%)	40.60	40.60	34.27	Fatheads	Soft Water	73
	38.62	38.62	32.00	Fatheads	Hard Water	73
	25.85	23.88	23.88	Bluegill	Soft Water	73
	49.86	49.13	44.49	Goldfish	Soft Water	73
o-Phthalic anhydride	Not found	Not found	Not found	Fatheads	Soft Water	73
	Not found	Not found	Not found	Fatheads	Soft Water	73
	Not found	Not found	Not found	Fatheads	Soft Water	73
Styrene (stabilized)	56.73	53.58	46.41	Fatheads	Soft Water	73
	62.81	62.81	59.30	Fatheads	Hard Water	73
	25.05	25.05	25.05	Bluegill	Soft Water	73
	64.78	64.74	64.74	Goldfish	Soft Water	73
	74.83	74.83	74.83	Guppies	Soft Water	73

TABLE VI-9 (Continued)

TOXICITY BIOASSAY RESULTS

Compound	TL_m (Median Tolerance Limit) 24 Hr (mg/1)	48 Hr (mg/1)	96 Hr (mg/1)	Test Animal	Remarks	Ref
Toluene reagent	46.31	46.31	34.27	Fatheads	Soft Water	73
	56.00	56.00	42.33	Fatheads	Hard Water	73
	24.00	24.00	24.00	Bluegill	Soft Water	73
	57.68	57.68	57.68	Goldfish	Soft Water	73
	62.81	60.95	59.30	Guppies	Soft Water	73
Vinyl acetate	24.00	24.00	24.00	Fatheads	Soft Water	73
	22.17	20.31	19.73	Fatheads	Soft Water	73
	39.19	39.19	39.19	Fatheads	Hard Water	73
	36.81	36.81	35.75	Fatheads	Hard Water	73
	18.53	18.00	18.00	Bluegill	Soft Water	73
	42.33	42.33	42.33	Goldfish	Soft Water	73
	31.08	31.08	31.08	Guppies	Soft Water	73
Xylene	28.77	27.71	26.70	Fatheads	Soft Water	73
	28.77	28.77	28.77	Fatheads	Hard Water	73
	24.00	24.00	20.87	Bluegill	Soft Water	73
	36.81	36.81	36.81	Goldfish	Soft Water	73
	34.73	34.73	34.73	Guppies	Soft Water	73

TABLE VI-9(Continued)

TOXICITY BIOASSAY RESULTS

Compound	TL_m (Median Tolerance Limit) 24 Hr (%)	48 Hr (%)	96 Hr (%)	Test Animal	Remarks	Ref
Waste caustic	0.039	-	-	Bluegill	20°C	87
General refinery	21	18	4.0	Bluegill	20°C	87
Sulfuric acid alkylation	0.4	0.4	0.1	Bluegill	20°C	87
Sodium sulfide	25 mg/1	25 mg/1	7.5 mg/1	Bluegill	20°C Hard Water	87
Sodium hydroxide	43 mg/1	42 mg/1	12 mg/1	Bluegill	20°C Hard Water	87
Sulfuric acid	49 mg/1	49 mg/1	15 mg/1	Bluegill	20°C Hard Water	87

of a compound or waste can never be demonstrated scientifically (Pickering and Henderson, 1966), it is necessary to provide a "safety factor" to the TL_M values obtained in the laboratory. The concentration of a waste discharged to a stream is usually one-tenth to one-half its median tolerance limit (Gloyna and Malina, 1962). It was found that chere was little significant difference in the 24-hour and 96-hour TL_M values for 10 of the 15 petrochemicals that were evaluated (Pickering and Henderson, 1966). This appears to be true for many of the compounds listed in Table VI-8. It appears from this data that many of the petrochemicals affect fish within a short period of time. Since most fish kills are usually the result of toxic material spills and because the toxic conditions are manifested so rapidly in the fish, it has been proposed that a much shorter time interval be used in the laboratory bioassay (Burdick, 1965). However, very little data are available when bioassays at time intervals shorter than 24 hours are considered.

The avoidance of polluted water by fish has been suggested as a toxicity parameter (Ishio, 1965). In this investigation a gradient tank was used to determine the discriminatory sensitivity of fish exposed to toxic chemicals. The median avoidance concentrations of some pollutants tested were found to correspond to their lowest lethal concentrations. However, several problems develop when avoidance is used as a parameter. In many cases fish do not reliable avoid lethal concentrations of some toxicants (Cairns, 1957). For example, most fish have been found to be attracted to alkaline water. Ammonia and copper salts, both of which are potentially toxic, were found to attract fish indirectly by chemical reactions which reduced the alkalinity (Ishio, 1965). Carp have been found to enter continuously an ammonia contaminated stream even though large numbers were killed (Beak, 1965). The toxicity bioassay is a valuable tool in the establishment of criteria for wastewater discharge as long as its limitations are known and considered.

CONVENTIONAL POLLUTIONAL PARAMETERS

There is a multiplicity of constituent chemicals responsible for the pollutional nature of petrochemical wastewater. Pollution cannot be measured in terms of quantitative levels of specific contaminating components, but rather by general methods of characterization. Many of the analytical techniques which are used to identify the classes of chemicals in a waste stream are complicated and expensive and, in the case of some compounds, quantitative methods of analysis are extremely difficult to perform. Pollutants such as tars, oils, and hydrocarbons are mixtures of many chemicals which are sometimes impossible to separate, identify, and quantify. The use of general pollutional parameters therefore provides a common yardstick for the assessment of the pollutional characteristics of an effluent stream. Total quantities of significant pollutants can be determined and waste streams from different processes compared with regard to their pollutional capacities by using these parameters.

The one manner of expressing waste characteristics is in terms of the ratio of quantity of pollutant produced to the quantity of product manufactured. Such comparison provides an accurate way of predicting effluent characteristics from any given petrochemical process. Virtually no published data of this type are available from the petrochemical industry, however, a limited amount of information regarding pollutants in relation to the output of thirty major products is presented in Appendix II. Information regarding major producers, projected production, uses, petrochemical conversion processes, and waste reduction by process change is also included. It is normally necessary to select data from unit process wastewaters which are typical of the industry. The characteristics of effluents from typical unit processes are listed in Tables VI-10 through VI-14. In most cases, these values are taken from a single plant and cannot be used as an absolute basis for predicting process waste characteristics from every plant. However, these values can be used to estimate the order of magnitude of the more important pollutional characteristics of unit process effluents and, as such, are useful in predicting effluent qualities.

Acidity

The acidity of a waste is a measure of the quantity of compounds contained therein which will dissociate in an aqueous solution to produce hydrogen ions. Acidity in a petrochemical waste can be contributed by both organic and inorganic compound dissociation. Most mineral acids found in petrochemical wastes (sulfuric acid, nitric acid, phosphoric acid) are typically strong acids. The most common weaker acids found in petrochemical wastes include the organic acids such as carboxylic acid and the inorganic acid, carbonic acid (H_2CO_3). Typical acid wastes from petrochemical processing and their acidity are listed in Table VI-12.

Alkalinity

Compounds which contribute to alkalinity in wastewaters are those which dissociate in aqueous solutions to produce hydroxyl ions. Alkalinity is often defined as the acid consuming ability of the wastewater and is measured by titrating a given volume of waste with standard acid until all of the alkaline material has reacted to form salts. In effect, alkalinity is the exact opposite of acidity; high alkalinities lower the hydrogen ion concentration of a solution and raise its pH.

Both inorganic and organic compounds can contribute to alkalinity, but the most important alkaline wastes in the petrochemical industry are the spent caustics containing sodium, calcium, and

TABLE VI-10

TYPICAL PROCESS WASTE CHARACTERISTICS OF PRIMARY CONVERSION AND REFINING PROCESSES

Characteristic	Crude Desalting	Catalytic Cracking	Naphtha Cracking	Sour Condensates from Distillation, Cracking, etc.
Ammonia (mg/1)	80	-	-	135-6,550
BOD (mg/1)	60-610	230-440	-	500-1,000
COD (mg/1)	124-470	500-2,800	53-180	500-2,000
Oil (mg/1)	20-516	200-2,600	160	100-1,000
pH (mg/1)	7.2-9.1	-	-	4.5-9.5
Phenols (mg/1)	10-25	20-26	6-10	100-1,000
Salt (as NaCl) (wt %)	0.4-25	-	-	-
Sulfides (mg/1)	0-13	-	-	390-8,250 (H_2S)
Reference	(15)	(33)	(15)	(15)

TABLE VI-11

TYPICAL SPENT CAUSTIC STREAM CHARACTERISTICS

Characteristics	Benzene Sulfonation Scrubbing	Orthophenylphenol Washing	Alkylate Washing	Polymerization	Various Refining Processes
Alkalinity (mg/l)	33,800	18,400	46,250	209,330	-
BOD (mg/l)	53,600	18,400	256	8,440	-
COD (mg/l)	112,000	67,600	3,230	50,350	-
H_2S (mg/l)	-	-	-	-	2,200-53,600
pH	13.2	9-12	12.8	12.7	-
Phenols (mg/l)	8.3	5,500	50	22.2	2,000-25,300
NaOH (wt %)	1	0.2-0.5	-	-	4.2-8.2
Na_2SO_4 (wt %)	1.5-2.5	-	-	-	-
Sulfates (mg/l)	3,760	2,440	-	-	-
Sulfides (mg/l)	-	-	2	3,060	-
Sulfites (mg/l)	7,100	4,720	-	-	-
Total Solids	90,300	40,800	-	-	-
Misc.	trace	trace OP-phenol			
Reference	(32)	(32)	(69)	(69)	(15)

TABLE VI-12

TYPICAL ACID WASTES CHARACTERISTICS

Characteristic	Acid Wash-Alkylation	Acid Wash-Phenol Still Bottoms	Acid Wash-Orthophenyl-phenol	Sulfite Wash Liq.OP-phenol Distillation
Acidity (mg/l)	1,105-12,325	-	24,120	675
BOD (mg/l)	31	20,800	13,600	105,000
COD (mg/l)	1,251	248,000	23,400	689,000
Dissolved Solids (mg/l)	-	340,500	81,300	176,800
Oil (mg/l)	131.5	-	-	-
pH	0.6-1.9	1.0	1.1	3.8
Phenols (mg/l)	-	3,800	1,500	16,400
Sulfate (mg/l)	-	-	54,700	-
Sulfite (mg/l)	-	34,800	2,920	74,000
Total Solids (mg/l)	-	403,200	81,600	176,900
Reference	(69)	(32)	(32)	(32)

TABLE VI-12 (continued)

TYPICAL ACID WASTES CHARACTERISTICS

Characteristic	2, 4 - D Acid Wash	2, 4, 5 - T Acid Wash
BOD (mg/l)	13,000-16,700	13,400-16,800
Chlorides (mg/l)	72,000-144,000	69,000-96,300
COD (mg/l)	22,700-27,500	19,600-25,700
Dissolved Solids (mg/l)	166,770	171,770
pH	8.5-9.5	7.5-7.9
Total Nitrogen (mg/l)	45	40
Total Solids (mg/l)	167,220	172,470
Total Volatile Solids (mg/l)	22,100	18,150
Reference	(37)	(37)

TABLE VI-13

TYPICAL PROCESS WASTE CHARACTERISTICS-MISCELLANEOUS

Characteristic	Nylon Manufacture	Synthetic Rubber	Butadiene (after API)
Alkalinity (mg/l)	22,500-40,700	37-40	370
Chlorides (mg/l)	475-3,340	2,670-2,800	1,275-1,350
COD (mg/l)	74,000-87,800	173-192	290-359
Oil (mg/l)	152-367	-	-
pH	7.4-12.0	6.4-6.7	8.4-8.5
PO_4 (mg/l)	5-78	19-22	38
SO_4 (mg/l)	0-194	1,425-1,470	910
TOC (mg/l)	19,600-37,200	97-110	131-165
Total Kjeldahl Nitrogen (mg/l)	4,630-10,500	74-89	63
Total Solids (mg/l)	41,700-123,500	7,420-12,000	3,730
Reference	(32)	(32)	(32)

TABLE VI-13 (Continued)

TYPICAL PROCESS WASTES CHARACTERISTICS-MISCELLANEOUS

Characteristic	Hexamethylene-diamine Mfr.	Adipic Acid Manufacture
Alkalinity (Total) (mg/l)	40,000-82,000	1,500-6,000
BOD (mg/l)	-	-
Chlorides (mg/l)	1,050-6,620	726-901
COD (mg/l)	23,400-65,800	112,600-169,800
Dissolved Solids (mg/l)	1,613-6,618	54,000-74,000
pH	10.2-10.9	4.1-5.2
Phenols (mg/l)	-	-
PO_4 (mg/l)	89-125	1-4
SO_4 (mg/l)	104-128	142-160
Total N (mg/l)	18,000-33,000	98-280
Total Solids (mg/l)	1,685-7,030	55,000-76,500
Misc. as Indicated	TOC = 7,500 - 20,400 mg/l	TOC = 29,200 - 80,000 mg/l
Reference	(32)	(32)

TABLE VI-13 (Continued)

TYPICAL PROCESS WASTES CHARACTERISTICS-MISCELLANEOUS

Characteristic	Olefin Production (After Oil Separator)	Olefin Production	Chlorinated Hydrocarbon Manuf.*	Synthetic Rubber Polymerization
Alkalinity (mg/1)	1,490	-		
Chlorides (mg/1)	-	-	116,000-123,000	550
COD (mg/1)	500-1,500	500-2,000	3,340	3,072
pH	9.8-10.0	4.0-8.5	12.6	7.8
Oil (mg/1)	-	10-300	-	-
Phenol (mg/1)	10-50	10-50	-	-
PO_4 (mg/1)	10	-	-	-
SO_4 (mg/1)	180	-	-	-
Sulfide (mg/1)	-	0-1	-	-
TOC (mg/1)	150-700	-	-	-
Total Kjeldahl Nitrogen (mg/1)	60	-	-	-
Total Dissolved Solids (mg/1)	-	5-100	-	-
Total Solids (mg/1)	2,140	-	-	-
Reference	(32)	(66)	(36)	(36)

TABLE VI-14

TYPICAL WASH WATERS CHARACTERISTICS (SCRUBBING PROCESSES)

Process	Orthophenylphenol Treating	Alkyd Scrubber Solution Resin Manufacture
Acidity (mg/l)	-	6,120
Alkalinity (mg/l)	296	-
BOD_5 (mg/l)	-	30,000
COD (mg/l)	-	37,100
Dissolved Solids (mg/l)	-	19,400
pH	9.1	2.1
Phenols (mg/l)	830	8.3
Total Solids (mg/l)	608	19,500
Misc. as Indicated		traces of pentaerythritol, phthalic anhydride, glycerine
Reference	(32)	(32)

potassium salts. These compounds present in such wastes tend to raise the pH to extremely high levels. The alkalinities of typical spent caustic streams are given in Table VI-11. Other process wastes may also contain significant amounts of alkalinity. Nitrogen in the ammonium form, for example, can contribute to the alkalinity of a solution.

The principal adverse consequences of high alkalinities in wastewater are biological, although caustic alkalinity, such as sodium or potassium, can cause embrittlement in boiler tubing.

Color and Turbidity

Color and turbidity are physical properties related to the concentration of certain solutes and suspended particles in wastewaters. Many of the wastes produced by the petrochemical industry contain color-producing compounds.

Color in wastewater, true and apparent, can be attributed to two types of physical phenomena. Certain materials in solution or suspension in water will absorb incident light and the wave lengths of visible light absorbed will determine the color of the liquid. The other color effect is caused by the scattering of incident light by colloidal or suspended materials, and liquids which exhibit this light-scattering effect are termed turbid. Both of these effects are highly undesirable in waters receiving waste effluents. Color and turbidity diminish light penetration in natural waters. This effect was discussed previously. Color and turbidity also affect the domestic use of water in that they must be removed prior to public acceptance. This removal process often adds great expense to water treatment costs.

Color in water is measured by comparing the sample with a standard cobalt-platinum solution. Turbidity is measured by using several different types of proprietary instruments which measure either scattered or transmitted light. Color which is caused by dissolved contaminants is often termed "true" color and color caused by petrochemical wastes is predominantly of this type. Color caused by suspended and colloidal material is referred to as "apparent" color.

pH

The hydrogen ion concentration in an aqueous solution is represented by the pH of that solution. The pH is defined as the negative logarithm of the hydrogen ion concentration in a solution. The pH scale ranges from zero to fourteen with a pH of seven representing neutral conditions, that is, equal concentrations of hydrogen and hydroxyl ions. Values of pH less than seven indicate increasing hydrogen ion concentration or acidity; pH values greater than seven indicate increasing basic conditions. The pH value is an effective parameter for predicting chemical and biological properties of aqueous solutions. It should be emphasized that pH is not a quantitative measurement and cannot be used to predict the quantities of alkaline or acidic materials in a water sample. However, most effluent and stream standards are based on maximum and minumum allowable pH values rather than on alkalinity and acidity.

Most living aquatic organisms, either plant or animal, function most effectively at neutral or near-neutral pH levels. Certain microorganisms, principally bacteria, can grow and proliferate at extremely high or extremely low pH values. Most other aquatic organisms can tolerate only brief exposures to high and low pH values before death ensues. The pH range generally required by most aquatic organisms is pH five to pH nine. Values outside this range will exert a toxic influence on much of the aquatic life; therefore, pH is a valuable indicator of the possible toxic effects due to excessive acidity or alkalinity of a waste effluent. The pH value also can serve as an indicator of the corrosive potential of a process effluent.

Most methods of measuring pH employ an instrument which determines an electric potential developed between two electrodes immersed in the solution to be tested. The most common of these instruments utilizes the glass-calomel electrode system. In special cases, special electrodes may have to be used to avoid interference by certain chemicals.

Organic Material

In order to predict the polluting potential of organic-laden wastewaters, it is necessary to employ some quantitative parameter. Since the oxygen demand of organic wastes presents one of the primary problems in organic waste control, the most commonly used parameters measure the chemical or biochemical oxygen demand potential of the wastes. These parameters are universally accepted although there are many limitations in their use and application. Recently a rapid and simple method of determining total organic carbon has been introduced which measures the polluting potential in terms of organic carbon present rather than molecular oxygen required. Such an evaluation is a valuable supplement to oxygen demand tests when categorizing a wastewater according to its organic polluting strength.

Biochemical Oxygen Demand - Biochemical oxygen demand (BOD) is a measure of the biologically oxidizable organic material in a waste. Ideally the Bod should represent the oxygen demand which is exerted during the microbial oxidation of organics in the waste, either in a biological treatment process or in a receiving body of water. The ultimate BOD is the oxygen required to biochemically oxidize all of the organic material to the less complex end-products. However, the ultimate BOD may not include all the BOD expected by nitrogen compounds. In practice, the BOD_5 is usually used for laboratory determinations of waste. This procedure is standardized and is described in detail in Standard Methods (1965).

Petrochemical wastes present certain problems when BOD is used as the pollution parameter. Certain compounds react chemically with free oxygen and create an immediate oxygen demand (IOD). Compensation for this demand must be included when using the BOD test. Certain organic compounds in petrochemical wastes are toxic at higher concentrations to microorganisms but exert high oxygen demands at nontoxic levels. Some inorganic compounds such as sulfides, chlorides, ammonia, and heavy metal salts may cause a toxic or deleterious effect in high concentrations and these effects must be taken into account by employing a sufficient dilution factor to prevent the toxic effects from occurring. Many of the chemicals present in petrochemical effluents are not normally present in nature; thus, it is necessary to use a microbial population which is properly acclimated to the specific waste under investigation if accurate BOD values are to be obtained.

Since BOD is the oldest and most common of the parameters used for estimating organic material, most effluent quality standards are based on a maximum allowable BOD effluent concentration. One disadvantage of BOD is that it measures only biologically degradable organics.

The BOD concentrations in effluents from typical petrochemical process wastes are listed in Tables VI-10 through VI-14. Typical effluent analyses from entire petrochemical plants are shown in Table VI-15. Wastes discharged from the petrochemical industry contain high concentrations of organic material, as indicated in these tables. The biochemical oxygen demand values of many important petrochemicals are given in Table VI-1.

Techniques to measure the BOD values in Table VI-1 should be mentioned. In nearly all cases sewage organisms were used as the source of microbial seed for the BOD test. The importance of using an acclimated seed for the measurement of the BOD values of complex organic compounds has been stressed. For example, the BOD_5 value of acrylamide monomer was determined using an acclimated seed and a sewage seed. The five-day BOD value obtained using the sewage seed was only 17 percent of the value obtained when a seed acclimated to the monomer was used (Cherry, et. al.,1956). Even a microbial seed which is acclimated to a compound closely related in structure to the test compound may not give the highest possible BOD value, which is of utmost importance. The BOD_5 values obtained from acrylamide monomer using a microbial seed acclimated to acrylonitrile were only 22 percent of the values obtained with a seed acclimated to the monomer (Cherry, et. al.,1956). Thus, the BOD values in Table VI-1 should be used only as a rough estimate of the ease of biodegradability of the compounds since some of the compounds probably will produce much higher BOD values if an acclimated seed is used.

TABLE VI-15

TOTAL PLANT EFFLUENT ANALYSES
TYPICAL PETROCHEMICAL PLANTS
(Process Waste Before Treatment)

Plant Products	Mixed Chemicals incl. ethylene oxide, propylene oxide, glycols, amines, and ethers	Refinery, Detergent Alkylate	Refinery, Butadiene, Butyl Rubber
Alkalinity (mg/l)	4,060	365	164
BOD (mg/l)	1,950	345	225
Chlorides (mg/l)	430-800	1,980	825
COD (mg/l)	7,970-8,540	855	610
Oils (mg/l)	547	73	-
pH	9.4-9.8	9.2	7.5
Phenols (mg/l)	-	160	17
Sulfates (mg/l)	655	280	-
Suspended Solids (mg/l)	27-60	121	110
TOC (mg/l)	-	-	160**
Total Nitrogen (mg/l)	1,160-1,253	89	48
Total Solids (mg/l)	2,191-3,029	3,770	2,810
Misc. as Indicated		Sulfide= 150 ppm *	PO_4=trace
Reference	(38)	(39)	(40)

---

* Cooling Water Excluded

** Filtered

TABLE VI-15 (Continued)

TOTAL PLANT EFFLUENT ANALYSES TYPICAL PETROCHEMICAL PLANTS

Plant Products	Mixed Organics	2,4,5-Trichlorophenol	2,4-Dichlorophenol	Nylon
BOD_5 (mg/l)	1,950	16,800	16,700	170
Chlorides (mg/l)	800	96,300	144,000	800
COD (mg/l)	1,972	21,700	27,500	2,000
Oils (mg/l)	547	-	-	45
Phenols (mg/l)	10-50	-	-	400
Suspended Solids (mg/l)	60	700	348	neg.
Total Nitrogen (mg/l)	1,253	40	45	100
Total Solids (mg/l)	3,029	172,467	167,221	3,000
Misc. as Indicated	SO_4 = 655 mg/l	% Vol. TS = 10.5	% Vol. TS = 13.2	H_2S = 12 mg/l
Reference	(31)	(37)	(37)	(31)

TABLE VI-15 (Continued)

TOTAL PLANT EFFLUENT ANALYSES
TYPICAL PETROCHEMICAL PLANTS

Plant Products	Phenols, Cresols
Alkalinity (mg/l)	192
BOD_5 (mg/l)	550-850
Chlorides (mg/l)	230
COD (mg/l)	990-1,940
Color (Color Units)	50
Hardness (mg/l)	250
IOD (mg/l)	17
Kjeldahl-N (mg/l)	trace
NH_3-N (mg/l)	trace
Oil (mg/l)	trace
pH	4.6-7.2
Phenols (mg/l)	280-550
PO_4 (mg/l)	3
Sulfides (mg/l)	trace-1
Suspended Solids (mg/l)	12-88
Temperature $^\circ C$	24.5
TOC (mg/l)	320-580
Total Solids (mg/l)	1,870-2,315
Reference	(44)

A thorough description of some chemical compounds which are resistant to aerobic biological stabilization is given by Ludzack and Ettinger (1960). The degradation of a number of different aromatic compounds by bacteria acclimated to phenol is discussed by Chambers, Tabak, and Kabler (1963). Many of the chemical compounds characterized in these two papers are found in petrochemical wastes.

Chemical Oxygen Demand - The oxygen required to chemically oxidize the organic compounds in a wastewater is termed the chemical oxygen demand (COD). Several COD testing methods are used, the most common one using potassium dichromate to oxidize the organic matter under acid conditions at a temperature of 180°C. This method completely oxidizes most organic compounds, which should represent the majority of organic materials in an effluent; however, a few of the more stable compounds in higher molecular weight materials are not measured. Benzene, for example, is a significant petrochemical pollutant and is not oxidized by any of the COD oxidants. The principal advantages of the COD test are the analytical time of two hours instead of five days, accuracy, and independence from temperature and acclimated seed considerations. COD is also valuable in the determination of the non-biodegradable portion of a waste, as indicated by the COD concentration when the corresponding BOD is zero or negligible.

Several disadvantages are inherent in the COD approach. There is no general correlation between the COD and BOD of petrochemical effluents; however, a COD-BOD correlation often does exist for a specific effluent, rendering COD a valuable parameters for a treatment process operation once this correlation has been established.

The interference of high chloride concentrations common to many petrochemical wastewaters may allude to erroneous COD determinations. These chlorides are oxidized by dichromate to chlorine:

$$Cr_2O_7^{=} + 6\,Cl^- + 14\,H^+ \longrightarrow 3\,Cl_2 + 2Cr^{+++} + 7\,H_2O$$

This interference can be minimized, however, by the addition of $HgSO_4$ to the mixture, as the Hg^{++} combine with Cl^- to form essentially non-ionized $HgCl_2$:

$$Hg^{++} + 2\,Cl^- \longrightarrow HgCl_2$$

If insufficient amounts of $HgSO_4$ are added to the mixture to prevent chloride oxidation, the excess Cl^- will precipitate the Ag^+ catalyst necessary to oxidize straight chain acids and alcohols:

$$Ag^+ + Cl^- \longrightarrow AgCl$$

From this discussion, it follows that the presence of excessive chlorides do interfere with the COD test and can result in either inordinately high or low readings, depending on the relative degrees of chloride oxidation and silver catalyst precipitation.

The COD values for some typical chemical wastes are given in Tables VI-10through VI-14.

Total Organic Carbon - Total organic carbon (TOC) is the measure of all organic carbon present in a waste. It is measured by completely oxidizing all of the organic material to carbon dioxide and water with a subsequent quantitative determination of the carbon dioxide released. The oldest procedure involved a wet combustion process which was difficult and time consuming. A method recently developed is rapid and accurate and insures complete organic oxidation by providing a pure oxygen environment, heat, and a cobalt catalyst followed by a quantitative analysis of the released carbon dioxide on an infrared spectrophotometer (Van Hall, et. al.,1963). This process may well become one of the more important methods of determining the organic content of wastewaters because it completely measures all organic compounds. However, like COD, there is no general correlation with BOD. There may or may not be a correlation between TOC and BOD for a specific waste stream; however, TOC can be used to measure treatment plant efficiency and monitor effluent streams whether or not this correlation exists.

Total organic carbon in combination with BOD and COD is probably the ideal method for determining the non-biodegradable fraction of an organic waste. The TOC parameter is particularly valuable for assessing the organic content of petrochemical waste since it is not affected by the interferences and variables prevalent in the COD and BOD procedures.

Since TOC is a relatively new approach, effluent quality data in terms of organic carbon is limited. Data presently available for some petrochemical process wastes are listed in Tables VI-10 through VI-14.

Total Oxygen Demand

Total oxygen demand (TOD) has recently been proposed as a waste strength parameter, primarily on the basis of the development of an automated analyzer. The TOC of an aqueous sample using this analyzer includes the total carbon, hydrogen, and nitrogen oxygen demand, although only a partial oxidation of sulfur compounds occurs. Total oxygen demand has been correlated in specific instances to chemical oxygen demand, and is a promising parameter in this respect (Clifford, 1967).

Immediate Oxygen Demand

Immediate oxygen demand (IOD) is exerted by compounds which react immediately with the dissolved oxygen when they are introduced into water containing oxygen. Such compounds include sulfides, thiosulfates, sulfites, nitrites, and aldehydes. The procedure for measuring IOD is standardized (Standard Methods for the Examination of Water and Wastewater, 1965)

Solids

Solid materials in wastewater effluents can be either organic or inorganic, dissolved or suspended. They consist of the materials which were described earlier under the chemical classifications.

Dissolved organic solids may cause color, taste, odor, and oxygen demand and are discussed under these headings. Inorganic dissolved solids are not particularly harmful or undesirable at lower concentrations. The main criteria for limiting dissolved solids include: tastes that are often produced by dissolved solids concentrations greater than 1,000 mg/l; high dissolved solids concentrations that may precipitate solids if the environmental conditions change; and high dissolved solids concentrations that may render water unfit for industrial uses such as boiler water (Beychok, 1967). The United States Public Health Service has set 1,000 mg/l as the maximum desirable total dissolved solids concentration in drinking water.

Some petrochemical process effluents, such as spent caustic effluents and acid wash wastes, have extremely high dissolved solids concentrations. Most of the solids in petrochemical wastes are present in the dissolved form. Suspended solids constitute the difference between total and dissolved solids and include colloidal materials which will not settle, even under quiescent conditions. Total and dissolved solids concentrations for typical process effluents are included in Tables VI-10 through VI-14.

Surface Activity

Surface-active agents are compounds which tend to concentrate at an interface, arranging their molecules so that they form a film along the interface. This surface-active property enables them to reduce the surface tension of liquids, emulsifying dirt and oily material (Stephenson, 1966). The principal use of surface-active agents is in synthetic detergents which have largely replaced soaps as cleaning agents. Unlike soaps, synthetic detergents do not form insoluble salts with calcium and magnesium ions, and they can therefore be used in hard water without the occurrence of undesirable precipitates.

The chemical characteristics of synthetic detergents are fully discussed elsewhere (Stephenson, 1966) and will be mentioned only briefly here. Surface-active agents contain two important functional groups, a water-soluble group and an oil-soluble group, giving the molecule its surface-active properties. The oil-soluble or hydrophobic group is usually a long-chain hydrocarbon containing eight to twenty-two carbon atoms. The water-soluble or hydrophilic group may be composed of one or four general types of polar groups: (a) anionic groups consisting of sulfonates, sulfates, and carboxylic acid groups; (b) cationic groups such as amine salts and ammonium compounds; (c) amphoteric groups in which the molecule contains both anionic and cationic groups; and (d) nonionic groups which do not ionize but are water soluble, such as alcohols and glycols (Stephenson, 1966).

Various laboratory procedures are available for the determination of synthetic detergents in water (Standard Methods, 1965). Other surface-active chemicals (sulfonic acids, carboxylic acids, etc.) must be determined by laboratory analyses which are not commonly used as pollutional parameters.

Taste and Odor

Methods used to classify and measure taste and odor in aquatic organisms are strictly arbitrary and most involve the use of human testers who determine the dilution required to make the taste and odor of a particular wastewater satisfactory. Since taste and odor are human senses, this is probably the most suitable method for their determination. Another possibility is the isolation, identification, and measurement of substances which cause taste and odor, but this procedure is currently impractical.

Temperature

Thermal pollution is a serious problem since elevated temperatures in receiving waters can cause deleterious effects. The primary effects are biological although downstream users may also suffer economically. Wastes from petrochemical industries are often discharged at high temperatures and may require precooling before treatment.

Toxicity

Many of the compounds and chemicals present in petrochemical wastes are toxic to aquatic life. Petrochemicals can also exert toxic effects on higher plants and animals and may render the wastewater unfit for agricultural or livestock use.

The bioassay technique is commonly used for measuring wastewater toxicity. The bioassay is used to determine the toxic concentration of a taste by the use of a dilution technique. Results obtained from a bioassay are usually reported in terms of the median tolerance level. Fish are the most commonly used test organisms, but new techniques are being developed which involve the use of other aquatic organisms such as algae and protozoa.

Oils

Oils are significant petrochemical pollutants. Total oil concentrations in the influents to biological treatment process should be limited to approximately 50 mg/l. Measurements will indicate which process streams will require oil separation prior to additional treatment.

Miscellaneous Pollutant Parameters

The aforementioned waste characteristics include the more commonly used methods for assessing pollutional effects of wastewaters, both petrochemical and other methods. However, more detailed descriptions of waste characteristics are often desired, particularly when treatment methods are being prescribed. There are several important parameters which are particularly important in the assessment of a petrochemical waste.

Phenols - Several methods are available for the measurement of phenols, the most common of them being the 4-aminoantipyrene procedure described in Standard Methods (1965). One disadvantage of this method is that certain phenolic compounds are not measured. Total phenols in aqueous solutions also can be determined by utilizing a differential ultraviolet absorption technique (Martin, et. al., 1967). This technique can be used for continuous monitoring of process effluents, and it measures all the phenolic compounds present in solution. Data showing the concentrations of phenolic compounds in some typical petrochemical process effluents are given in Tables VI-10 through VI-14.

Inorganic Ions - In certain cases, it is desirable to know the concentration of certain inorganic ions such as chlorides, phosphates, nitrates, and sulfates. Phosphates and nitrates, for example, are important biological nutrients, and the concentration of these ions in wastewaters to be treated biologically is of considerable importance in the design and operation of the treatment unit. Standard analytical techniques are used to measure inorganic ions in wastewater (Standard Methods., 1965).

Nitrogen must be present in its most reduced form, ammonia or ammonium ion, to be available to most bacteria in an optimum biological treatment system; however, many algae utilize nitrogen as nitrate. The nitrogen required for an efficient biological treatment process for nitrogen deficient petrochemical wastes can be calculated if the nitrogen content of the waste stream is known. The most common method is the Kjeldahl method described in Standard Methods (1965). In this technique, the organic nitrogen is converted to ammonia nitrogen which is then measured either by titration or colorimetric procedures.

Volatility - Some of the organic and inorganic compounds in petrochemical wastes are highly volatile and are subject to air-stripping. The volatility of a compound is a function of both its solubility and its vapor pressure. Volatile petrochemicals include the aldehydes, ketones, alcohols, and ethers. Several studies have shown the rate of air-stripping of some volatile organics which may be found in petrochemical wastes (Gandy, et. al., 1961; Englebrecht, et. al., 1961; and Gandy and Englebrecht, 1960). Volatility tests on petrochemical wastes involve the aeration of a waste sample at a given temperature, noting the removal of organic material within a specified time and using a parameter such as COD.

Heavy Metals - Waste streams with potential heavy metal contaminants are usually analyzed to determine the concentration of these metals and thereby establish the potential toxicity. Several techniques for heavy metal analysis are given in Standard Methods (1965). Atomic absorption flame photometry can also be used quantitatively to determine small quantities of metals. This method is based on the measurement of light absorbed at a given wave length by the unexcited atoms of the element being analyzed (Willard, et. al., 1965). Quantities of some metals in concentrations lower than one mg/l can be detected by this procedure.

Total Plant Effluent Analysis

Petrochemical plants use some or all of the unit processes which have been described. The many possible combinations of unit processes which can be and are being used in petrochemical plants make it impossible to correlate the effluent characteristics among plants. Intra-plant differences in the effluent segreatation systems; in-plant pretreatment systems; and process design, operation, and maintenance also contribute to the variations. The ideal method for predicting petrochemical wastewater characteristics would be to relate the quantity of pollutant produced by a unit process to production units, although enough data to develop these relationships is not available at the present time. Instead, the effluent analyses from several typical petrochemical plants are given in Table VI-15.

These data give a general idea of the variability of effluent characteristics in the petrochemical industry, although basic similarities are recognizable. In general, the pH values are greater than pH seven and these high values suggest the influence of the many caustic wastes employed in petrochemical processes. The effect of spent caustics is also reflected in the high total solids and low suspended solids concentrations of the wastewaters. This indicates that most of the solids in petrochemical wastewaters are in dissolved form. The data in Table VI-15 demonstrate that each petrochemical waste must be analyzed separately to predict its pollutional effects.

IDENTIFICATION AND MONITORING METHODS

There are many petrochemicals which cause marked adverse effects on the environment, even in extremely small concentrations. Standard analytical tools used for wastewater analysis (COD, BOD, etc.) are inadequate for evaluating these effects and for predicting their occurrence. New analytical methods must be developed so that low-level contaminants can be traced from the petrochemical processes, through the waste treatment system, and into the aquatic environment. If compounds causing taste, odor, and toxicity can be identified and traced to their source, methods for removing these persistent compounds from the wastewater then can be developed. The two general types of analytical procedures are chemical techniques and biological methods. Chemical techniques are used principally to measure low-level contaminants which cause color, taste, and odor while biological methods are used to observe toxic or inhibitory effects of waste discharges on the aquatic biota.

Chemical Methods of Analysis

This discussion considers the analyses of organic and inorganic pollutants. The following techniques do not represent all of the analytical methods which are used in water analysis, but include those which are frequently utilized or may be particularly applicable in the analysis of petrochemical wastes.

Inorganic Chemicals - A variety of analytical methods are available for analyzing the inorganic ions in water. A good review of these analytical techniques is available in the annual reviews of *Analytical Chemistry*.

Inorganic analyses often require two steps: a separation and/or concentration step followed by the identification and quantification of the desired compound. When possible, it is simplest to obtain a direct measure of a compound in the aqueous sample.

However, some type of separation procedure is usually required to remove other interfering substances from other compounds to concentrate the desired compound to measurable quantities. The separation processes most often used for inorganic compounds are volatilization, precipitation, liquid-liquid extraction, and adsorption (Mellon, 1960). Chromatography and ion exchange are the two most commonly used adsorptive methods of separation.

Gravimetric procedures are often used if the compound in question can be isolated and maintained in a measurable form (Mellon, 1960). Several gravimetric procedures for determining inorganic compounds, including methods of analysis for potassium, sodium, calcium and silica are described in Standard Methods (1965). Gravimetric procedures are time-consuming, difficult, and are normally not used if other techniques are applicable.

Titrimetric methods are used for several inorganic analyses, the most common of which measure alkalinity, acidity, and calcium and magnesium ions using ethylene diaminetetracetic acid (EDTA). New detectors have been developed to define more precisely the end-point of the titration reaction. These detectors utilize potentiometric, photometric, and conductometric methods in determining the reaction end-point.

Spectroscopic methods are also used to measure many inorganic compounds. Flame photometry can be used to measure the alkali and alkaline earth metals such as sodium and potassium (Anon., Standard Methods, 1965). This method is simple and the equipment is relatively inexpensive. Emission spectroscopes using high temperature arcs and rarefied gases can be used to measure metals in the parts per billion concentration range (Mellon, 1960). Atomic absorption spectroscopy is another form of absorption spectroscopy which can be used for trace metal analysis.

Absorption spectrometers are available for measuring absorption in almost all regions of the electromagnetic spectrum. These methods can be used to identify and measure inorganic compounds from trace concentrations to fairly large quantities. In aqueous samples, interferences are common, and separation procedures must often be employed to eliminate these problems.

Most of the inorganic analyses employing the ultraviolet and visible ranges of the spectrum involve the measurement of chemical complexes of the inorganic compounds. Many colorimetric methods used for determining the concentration of inorganic ions are listed in Standard Methods (1965). The sensitivity of some of the spectrometric techniques for inorganic compounds approaches one part per billion (Mellon, 1960).

Infrared spectroscopy can also be used to measure inorganic compounds, but has not been used extensively in water analyses (Mellon, 1960).

One reason for this is that all water must be removed from a sample prior to analysis, since water strongly absorbs across the entire infrared spectrum. Gamma-ray and x-ray spectrometry have also been used to a limited extent in water analysis.

Methods involving the measurement of the electrical properties of systems are also used for inorganic analyses of aqueous systems. Polarography, in which a potential is imposed across two electrodes immersed in the test solution measuring the resultant current, is probably the most commonly used electrometric analysis for inorganics. Methods have been standardized which can be used to determine simultaneously copper, lead, cadmium, zinc, and nickel (Anon., Standard Methods, 1965). Polarographic methods for measuring heavy metals are more rapid than the corresponding colorimetric methods and avoid many of the interferences; additionally, dissolved oxygen can be measured using several polarographic techniques.

Potentiometry and coulometry have also been proposed as tools for water analysis, but have not been extensively used in the identification of inorganic constituents of a wastewater. A well-known use of potentiometry is in the pH measurement.

Other methods are also available for measuring inorganic compounds of specific types and under specific conditions. For example, radioactivity measurements can be used to detect the presence of radioactive isotopes present in very low concentrations. However, it is doubtful that this method would be applicable for identifying most compounds present in a petrochemical waste. More research into the analysis of wastewaters may demonstrate the utility of these techniques.

None of the methods presented are universally applicable since they are dependent on the compound to be determined and the wastewater to be analyzed. The analyst will often find that he will need to use two or more analytical techniques to complete the analysis.

Organic Chemicals - Minute quantities of solubilized organic compounds can cause toxic effects, tastes, odors, foaming, and fouling of ion-exchange resins. Therefore, it is desirable to identify and quantify these organics and this has been the objective of much research.

Prior to analysis, most organic compounds in natural waters must be concentrated, and for some analyses, separated. The concentrations of organic contaminants in receiving waters are usually so low that they cannot be measured directly. Process effluents, however, do not often require concentrating the organic pollutants prior to analysis.

Several methods are available for concentrating trace organic compounds, including adsorption on carbon filters, liquid-liquid extraction, freeze concentration, distillation, and combinations of the techniques (Baker and Malo, 1967). These procedures must not alter the structure or relative distribution of the organic molecules subject to analysis. The adsorption of organic compounds on activated carbon filters is probably the best-known and most commonly used method of organic concentration. The organic compounds are removed from the carbon with a suitable solvent, usually chloroform. The extract is separated into the four fractions of strong acids, weak acids, basic, and neutral fractions using differential solubility techniques. These fractions can then be subjected to the various analytical methods for quantitative analysis. The carbon absorption procedure is used by the United States Public Health Service in its water quality surveillance network and is described in detail in Standard Methods (1965). Several papers have described the use of this technique for the determination of trace organics in natural waters (Braus, et. al.,1951; Lively, et. al.,1965; Middleton and Lichtenberg, 1960). The greatest disadvantage of the carbon adsorption method is that not all of the organic compounds are uniformly adsorbed and desorbed. Some chlorinated hydrocarbons have been completely recovered, while phenol, for example, is completely adsorbed but only 70 percent is desorbed from the carbon (Baker and Malo, 1967). Oxidation and biodegradation of organic compounds on the carbon surface has also been shown to occur (Hoak, 1964), and volatile organic compounds may be lost from the carbon prior to extraction. This volatilization of low boiling point organic compounds can be prevented if the carbon is kept wet and is extracted with the solvent without prior drying. Because of the limitations of the carbon adsorption procedure, particularly for quantitative analysis, other methods of organic analysis have been investigated.

Liquid-liquid extraction can be used effectively to concentrate certain organic compounds. The quantitative recovery of organic compounds from water is based on the affinity of the selected solvent for the organics. This procedure is considerably more rapid than the carbon adsorption technique and should eliminate the problems of organic structure alteration which have been attributed to the carbon filter technique. Both batch and continuous countercurrent extraction columns have been used, and ethyl ether is the most commonly used solvent (Hoak, 1964; Baker and Malo, 1967). Extremely small quantities of organics have been recovered using extraction procedures employing diethyl ether solvent which was subsequently vacuum evaporated to one milliliter (Caruso, et. al.,1966). Solvent extraction has still not replaced carbon adsorption since it is also subject to several problems. The principal problem involves the selection of a solvent which has an affinity for most organic compounds but which is readily separable from water. Separation of the solvent from water is the biggest limitation of the extraction process.

Freeze concentration methods have not yet found wide application in water analysis. The biggest advantage of organic concentration by freezing is that organic compounds are completely unaltered during the process. The effectiveness of freezing techniques is dependent upon the rates of freezing, the ionic concentration of the sample, and the type of organic compounds in the sample, The freezing technique is not yet fully developed but offers an attractive method for concentrating trace organics when it is perfected. Several examples of the application of freeze concentration techniques to aqueous samples have been suggested (Baker and Malo, 1967).

Distillation is the oldest concentration technique used in trace organic analysis, but is difficult toapply if the organic compounds being concentrated are volatile or heat labile. If the organics are stable under heating and are not volatile, distillation is probably the easiest method for concentrating them. The distillation procedure for concentrating phenols is a good example (Anon., Standard Methods 1965). Often it is impossible to concentrate all of the desired organic compounds by a single technique. Two or more concentration techniques often can be used in combination to produce measurable quantities of the contaminant in question.

Many of the analytical methods used to determine trace quantities of organic materials in water are the same as the techniques employed in inorganic analysis. The two most commonly used organic analytical techniques are spectroscopy and chromatography. For most of these procedures, it is necessary first to concentrate the sample using one of the methods previously described. In certain instances, small quantities of organic compounds can be determined directly without any preparatory procedures. These direct methods are most applicable for continuous monitoring of trace organics in waste effluents and receiving waters.

Spectroscopic techniques are probably the most commonly used methods of organic analysis, the principal ranges of the spectrum used for these analyses being the ultraviolet range, the visual range, and the infrared range.

Ultraviolet spectroscopy is often used in water and wastewater analysis. Generally it is difficult to determine the molecular structure of unknown compounds by ultraviolet analysis, since the ultraviolet-absorbing groups in a compound are usually affected by one another and discrete absorption bands do not often occur (Baker and Malo, 1967). Differential spectroscopy can be used to eliminate interferences by other compounds in a wastewater sample. A procedure has been developed which can be used to determine total phenols in aqueous solution (Martin, et. al.,1967). This is a differential absorption method based on the measurement of the phenolate ion which is formed in alkaline solutions of phenols. A neutral solution of sample is used as the blank. This procedure is considerably more rapid and less difficult than the standard colorimetric procedures because it measures total phenols which the colorimetric methods do not. No separation methods are required prior to analysis since differential absorption eliminates most interferences, and it is applicable to continuous monitoring of effluent streams. This procedure for measuring total phenols is presently being standardized by the ATSM Committee on Industrial Water (Baker and Malo, 1967).

Spectroscopy in the visual range, also known as colorimetry, is widely used in organic analyses. Most of these colorimetric methods are based on measuring a colored complex formed when the organic compound is chemically treated. The colored complexes produced are measured by differential absorption compared to reagent blanks which contain all of the color-producing reagents but not the organic compound. The phenol procedure (4-amino antipyrene method, Standard Methods, 1967) is sensitive to phenol concentrations in the microgram per liter range, provided that the sample is properly prepared. These colorimetric methods are nonspecific, and great care must be taken to eliminate possible interfering compounds (Baker and Malo, 1967).

Infrared spectroscopy is finding increased application in water analysis. Infrared techniques are usually used in combination with other analytical procedures to identify the molecular structure of organic contaminants. Functional groups in organic molecules absorb infrared light at various discrete wavelengths, providing a means for identifying them. Differential absorption techniques are usually used in infrared spectroscopy, and samples can be analyzed in the solid, liquid, or gaseous form. The use of long-path infrared sample cells for the analysis of gases makes infrared spectroscopy an excellent method for the study of odors (Baker, 1961). Infrared spectroscopy has been used extensively to analyze carbon adsorption extracts obtained in the National Water Quality Monitoring Network (Middleton and Lichtenberg, 1960).

Mass spectroscopy, in combination with other analytical techniques, has also been used to elucidate the structure of organic contaminants. The equipment required for mass spectroscopy is expensive which has limited its use to a few research laboratories (Baker and Malo, 1967). It offers several advantages in that it can provide a rapid means of identifying extremely small amounts of organics.

Gas-liquid chromatography is another analytical tool used in water analysis. The development of the sensitive flame-ionization, electron-capture, and electron-affinity detectors has made gas-liquid chromatography applicable for identifying most classes of organic compounds (Baker and Malo, 1967). The flame ionization detector has the added advantage of being insensitive to water, allowing the direct injection of aqueous samples into the chromatograph. This eliminates the time-consuming preparatory procedures required to eliminate interference due to water and permits the use of continuous monitoring techniques.

Many applications of gas-liquid chromatography to water analysis are mentioned in the literature. Baker and Malo (1967) give an excellent discussion of some of these applications. Gas-liquid chromatography techniques have been used extensively in pesticide analyses. Electron-capture detectors are used to identify the organic phosphate, chlorinated hydrocarbon, and organic sulfur pesticides in the microgram per liter concentration range. The flame-ionization detector has been used to measure many different organic compounds in aqueous samples. The sensitivity of this detector encompasses the microgram per liter to milligram per liter concentration range, depending upon the organic compound being analyzed. One of the most promising uses of gas-liquid chromatography and the flame-ionization detector is in the continuous monitoring of process and treatment plant effluents. A system of this type has been developed and is presently used at a chemical plant in West Virginia (Cochran and Bess, 1966). In one instance this system was used to discover a malfunctioning distillation unit by tracing an abnormal discharge of butanol to the unit. It was determined, however, that interferences in this analytical technique occurred in some process effluents, which precluded their sampling by continuous monitoring procedures. New types of column packings and changes in column temperature programming are being investigated to eliminate problems such as these. Gas-liquid chromatography probably offers the best possibility for continuous monitoring of any of the present analytical techniques.

Gas-liquid chromatography has been used extensively to separate organic compounds which are subsequently analyzed by other techniques such as mass spectroscopy.

Both thin-layer and paper chromatography have been used to some extent for the determination of trace organic compounds in water. Paper chromatography has been used to separate and identify pesticides in polluted streams in quantities as small as 0.1 mg/l (Baker and Malo, 1967). R. D. Hoak (1964) identified a number of compounds, including phenol, guiacol, m-cresol, 3-5 xylenol, and a number of aliphatic acids, in extracts from river water and oak leaf fermentations. Some compounds can be separated and identified in microgram per liter concentrations by paper chromatography. The principal disadvantages of paper chromatography are that is is a slow procedure and it is not extremely accurate for quantitative measurements. Thin-layer chromatography, however, has the separation powers of paper chromatography combined with the speed of gas chromatography.

A number of compounds have been separated by these techniques, including aldehydes, ketones, phenols, and a number of herbicides (Baker and Malo, 1967). The two chromatographic procedures, paper and thin-layer, are effective research tools for identifying trace organic compounds in water; however, they must be used in conjunction with other analytical and preparatory techniques and are not presently applicable for continuous monitoring. Combinations of the more important analytical techniques used in the identification and measurement of trace organics in water samples are often used, as a few brief examples will illustrate. Infrared spectroscopy, nuclear magnetic resonance, and gas chromatography-mass spectrometry have been used to quantify the structure of some products derived from petrochemicals (Butler, et. al.,1967). Carbon absorption, liquid-liquid extraction, silicagel adsorption chromatography, and gas chromatography were used to identify petroleum products in four water pollution incidents (Lively, et. al.,1965). The routine analysis of carbon column extracts from the National Water Quality Surveillance Network involves the use of solubility differentiation, gas chromatography, and infrared spectroscopy to identify the organic contaminants in surface waters (Middleton,and Lichtenberg, 1960). Some of the compounds identified by the United States Public Health Service in these surveys include DDT, O-nitrochlorobenzene, nitriles, substituted aromatics, phenols, detergents, organic acids, ketones, aldehydes, alcohols, and amines. The identification of trace organics or even fairly large amounts of organics in water samples is a difficult analytic problem. The choice of the analytical technique must be based on the nature of the compound to be measured, its concentration, and the presence of possible interfering organics or inorganics. An investigation was undertaken to develop laboratory techniques for efficiently selecting gas-liquid chromatograph operating parameter which are most suited to each type of petrochemical wastewater analysis problem. A set of optimum conditions was developed for measuring selected trace organics at levels at least down to one mg/l using direct aqueous injection. The practical means of applying these techniques, as opposed to theoretical considerations, was emphasized. Means of obtaining spectrometric confirmation of organic components with and without preconcentration by freeze-out and carbon adsorption also were studied. The resulting sequence of procedures for identification and measurement of the organics is illustrated in Figure VI-1 (Sugar and Conway, 1968). Future research should develop more and better techniques for estimating and evaluating the effects of trace organic compounds in water.

Biological Methods

Problems involved in the toxicity bioassay and the use of algae as toxicological indicators or any other laboratory method arise when trying to translate and interpret results as they actually apply to field conditions. Because of this uncertainty, safety

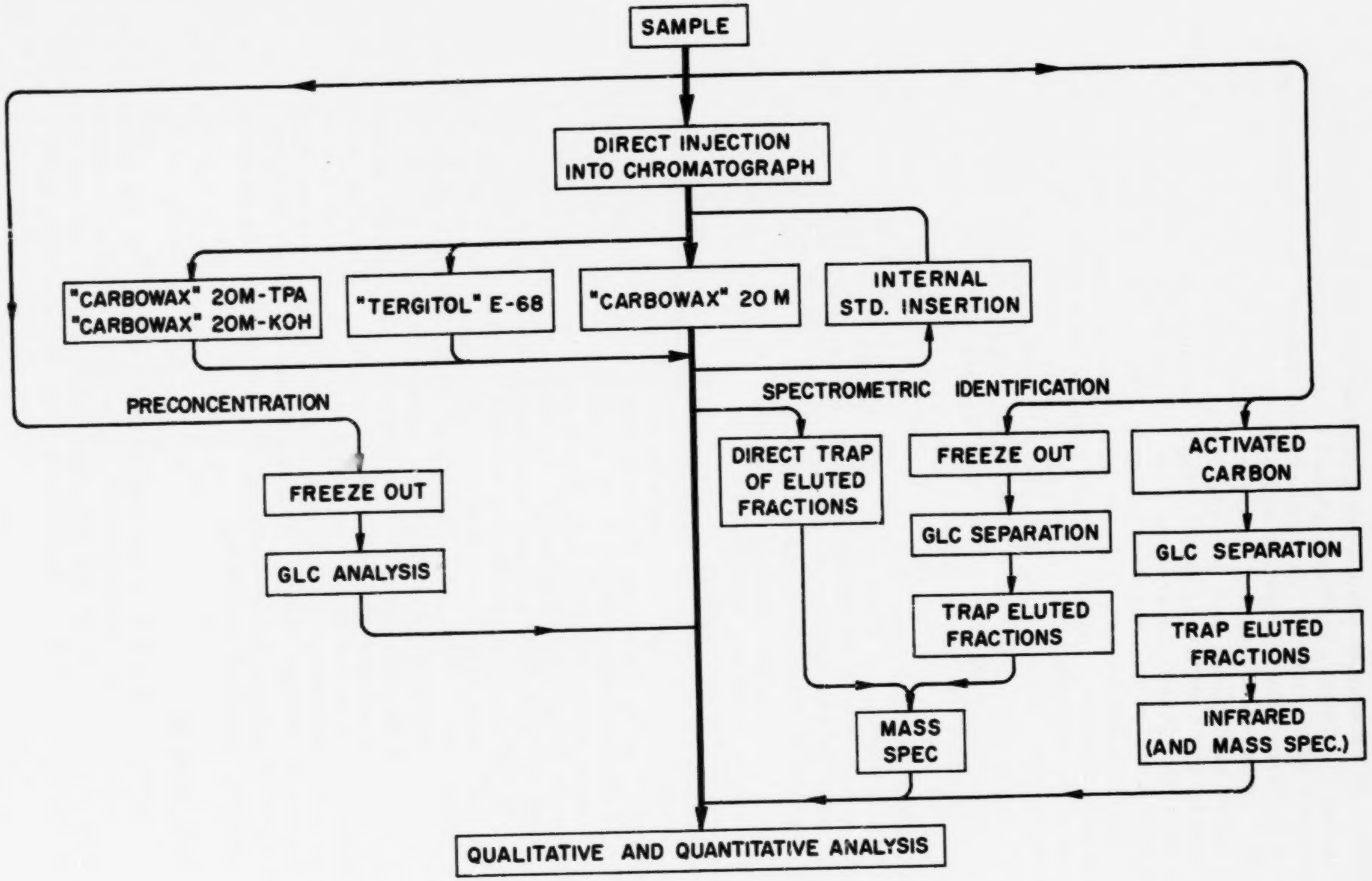

SAMPLE
DIRECT INJECTION INTO CHROMATOGRAPH
"CARBOWAX" 20M-TPA
"CARBOWAX" 20M-KOH
"TERGITOL" E-68
"CARBOWAX" 20 M
INTERNAL STD. INSERTION
PRECONCENTRATION
FREEZE OUT
GLC ANALYSIS
SPECTROMETRIC IDENTIFICATION
DIRECT TRAP OF ELUTED FRACTIONS
FREEZE OUT
GLC SEPARATION
TRAP ELUTED FRACTIONS
MASS SPEC
ACTIVATED CARBON
GLC SEPARATION
TRAP ELUTED FRACTIONS
INFRARED (AND MASS SPEC.)
QUALITATIVE AND QUANTITATIVE ANALYSIS

FIGURE VI-1

SCHEME FOR IDENTIFICATION OF TRACE ORGANICS

(Reference 79)

factors are used when laboratory results are transposed to field conditions. In addition, long-term effects of nonlethal concentrations of chemicals on the biota cannot be predicted in the laboratory. Effects on other members of the food chain cannot be evaluated by measuring toxicity on only one organism, but then it would obviously be impossible to measure the effects on each and every organism. For these reasons, procedures have been proposed which can be used to measure the biological effects of a waste in the aquatic environment in situ. The continuously operating biological systems have two advantages over their chemical monitoring systems counterpart: namely, (a) the biological system monitors the entire environment rather than preselected portions, and (b) the biological system considers all of the environmental variables while the chemical system records each characteristic separately (Cairns, 1965).

Most of the proposed biological techniques for measuring the effects of pollution in the environment are based on changes in the dominant species which occur in the receiving waters when pollutants are added. By studying the aquatic organisms upstream and downstream from the source of pollution, the changes in the ecosystem due to the pollution can be evaluated. One method for evaluating these effects is by measuring the changes in the population structure of the various aquatic communities. Severe pollution inevitably results in a reduction of the total number of species, although this reduction may be accompanied by an increase in the population of one particular species (Cairns, 1965). Normally the change in population will only be measured for several species of organisms.

For continuous monitoring purposes, it is desirable to utilize indicator organisms with relatively short life cycles so the response time will be relatively short. Diatoms, for example, can be effectively used as an indicator organism since they reproduce several times a day, will establish themselves on almost any type of sampling surface, and 150 to 180 species are usually present in unpolluted water (Cairns, 1965). It is desirable to have a large population, both in number and species, to give statistical accuracy to the monitoring system. Diatometers, which consist of suspended glass slides, can be placed in the subject water and will indicate any changes in the environment by the relative number of diatomites present in each species.

Another environmental biological monitoring system assigns a "biotic index" to the natural waters receiving pollutants (Beak, 1965). This biotic index is based on the macro-invertebrate organisms (insects, tubificial worms) in the receiving waters and can be calculated from samples taken by any method which gives an accurate representation of population densities. Six distinct stages of the index are proposed ranging from natural conditions to situations of severe pollution. The study of macro-invertebrates can also be used to observe the recovery of a stream from pollution, and there are several examples of its use involving industrial effluents (Hynes, 1965).

Bioassay techniques using organisms other than fish have also been proposed. These procedures are necessary since it is now realized that toxic effects of a compound on aquatic plants and invertebrates are equally as important as their effects on fish. The use of bacteria and microcrustaceans in toxicity determinations has been proposed (Willingham, and Andersen, 1966). Bacterial toxicity could be evaluated by using the change in oxygen uptake of aerobic bacteria or the change in luminescence in bioluminescient bacteria. Microcrustaceans may prove useful for toxicity determinations since they are easy to maintain in the laboratory and their phototactic or heartbeat change is easily detected. The use of the bacteria, protozoa, and algae present in the Winogradsky column has also been suggested as a toxicity indicator (Hutner, et. al., 1965). These organisms could be used to provide sensitive indicators of the efficiency of biological treatment systems by employing Winogradsky columns innoculated from the fauna of the biological system.

Protozoa are also effective indicators of the toxic effects of chemicals (Hutner, et. al., 1965). Several bioassay techniques have been used with protozoa as the indicators of toxicity. For example, Paramecium can be used to identify polynuclear benzenoid carcinogens (Hutner, et. al., 1965). This test is highly specific and very sensitive and depends upon the carcinogen-sensitized destruction of Paramecia by ultraviolet light. Conventional growth inhibition studies similar to those used with bacteria and algae are also common.

The conventional toxicity bioassay is undergoing changes. Many bioassays are now being performed with time periods of several months, in order to evaluate the chronic effects of chemical pollutants (Cairns, 1965). Also, other indicators rather than death are being used as the end-point of the bioassay, including changes in respiration, cruising-speed abilities, and other behaviors (Cairns, 1965). These changes should help to make the results of the bioassay more applicable and realistic.

Another type of biological measurement which should be mentioned is the panel test for taste and odor evaluation. These tests are used to determine the threshold odor number of a waste which is the dilution required to reduce the odor to barely detectable limits. These methods are based on a subjective estimate of odors by a panel, preferably trained in odor detection and are described in Standard Methods (1965). Attempts have been made to develop qualitative tests by preparing lists of terms describing odors and by using standard odors as references (Rosen, 1966). In general, these methods have been relatively unsuccessful since many variations and combinations of odors are possible. However, developing a successful method of odor characterization will be necessary if odor data from one source is to be used elsewhere (Baker, 1963).

It would be desirable if some chemical or mechanical means of measuring the intensity and character of odors was developed. but as of now there is no device available which appraoches the sensitivity of the natural sense of smell. Until these methods are developed, panel testing will probably remain the principal method of odor measurement.

These procedures represent only a few of the possible methods of biologically analyzing the effects of pollution. More research is needed to develop new methods and perfect the present ones so that the optimum water quality criteria, which will satisfy the needs of both the regulatory agencies and industry can be formulated and made workable, resulting in a more pollution-free environment.

REFERENCES - CHAPTER VI

1. Alabaster, J. S., "The Effect of Heated Effluents on Fish," Advances in Water Pollution Research, Vol. I, Macmillan Co., p. 261, New York, N. Y. (1964).

2. Anon., Committee Report, Task Group 245, or "Survey of Ground Water Contamination and Waste Disposal Practices," J. AWWA, v. 52, p. 1211 (1960).

3. Anon., Drinking Water Standards, U.S.P.H.S. Publ. No. 956, U. S. Department of Health, Education, and Welfare, Public Health Service (1962).

4. Anon., Manual on Disposal of Refinery Wastes, Vol. I, "Waste Water Containing Oil," American Petrol. Inst., New York, N. Y. (1953).

5. Anon., Manual on Disposal of Refinery Wastes, Vol. I , "Chemical Wastes," American Petrol. Inst., New York, N. Y. (1958).

6. Anon., Oxygen Relationships in Streams, Seminar Proceedings, R. A. Taft, San. Engr. Center Tech. Rept. W58-2, Cincinnati, Ohio (1958).

7. Anon., Society of Chemical Industry, Symposium, Geneva, May 2-3, 1957, "Molecular Structure and Organoleptic Quality," Monograph 1, Macmillan Co., New York, N. Y. (1957).

8. Anon., Standard Methods for the Examination of Water and Wastewater, American Public Health Assoc., New York, N. Y., 12th Edition (1965).

9. Anon., Water in Industry, Natl. Assoc. of Manufacturers and the Chamber of Commerce of the U. S., New York, N. Y. (1965).

10. Bacon, H. E. and Lewis, W. J., "Interference of Organic Contaminants with Ion Exchange Processes - Occurrence, Prevention, and Cost," Combustion, v. 32, p. 37 (July, 1960).

11. Baker, R. A., "Odor Effects of Aqueous Mixtures of Organic Chemicals," J. WPCF, v. 35, n. 6, p. 728 (June 1963).

12. Baker, R. A., "Problems of Tastes and Odors," J.WPCF, v. 33, n. 10, p. 1099 (Oct. 1961).

13. Baker, R. A. and Malo, B. A., "Water Quality Characteristics-Trace Organics," ASCE-Proc., v. 93 (J. San Engr. Div.) n. SA6, p. 41 (Dec. 1967).

14. Beak, T. W., Discussion of "Behavior of Fish Exposed to Toxic Substances," Advances in Water Pollution Research, V. I, p. 38 (1965).

15. Beychok, M. R., Aqueous Wastes from Petroleum and Petrochemical Plants, John Wiley & Sons, London (1967).

16. Braus, H., et. al., "A Study of the Concentration and Estimation of Organic Chemical Compounds in Raw and Filtered Surface Water," Anal. Chemistry, v. 23, p. 1160 (1951).

17. Burdick, G. E., "Some Problems in the Determination of the Cause of Fish Kills," Biological Problems in Water Pollution - Third Seminar 1962, R. A. Taft Sanitary Engr. Center, Cincinnati, Ohio p. 289 (1965).

18. Burttschell, R. H., et. al., "Chlorine Derivatives of Phenol Causing Taste and Odor," J. AWWA, v. 51, n. 2, p. 205 (Feb. 1959).

19. Butler, P. E., et. al., "Modern Instrumental Techniques in Structure Elucidation of Products Derived from Petrochemicals," Environ. Sci. & Tech., v. 1, n. 4, p. 315 (April 1967).

20. Cairns, J., Jr., "Environment and Time in Fish Toxicity," Ind. Wastes, v. 2, n. 1, p. 1 (Jan,, Feb. 1957).

21. Cairns, J., Jr., "Biological Concepts and Industrial Waste Disposal Problems," Proc. 20th Ind. Waste Conf., Purdue Univ., p. 49 (1965).

22. Cairns, J., Jr. and Scheir, A., "The Relationship of Bluegill Sunfish Body Size to Tolerance for Some Common Chemicals," Proc. 13th Ind. Waste Conf., Purdue Univ., p. 243 (1958).

23. Caruso, S. C., Bramer, H. C. and Hoak, R. D., "Tracing Organic Compounds in Surface Streams," Air and Water Poll. Int. J., v. 10, n. 1, p. 41 (Jan. 1966).

24. Cherry, A. B., Gabaccia, A. J. and Senn, H. W., "The Assimilation Behavior of Certain Toxic Organic Compounds in Natural Water," Sew. and Ind. Wastes, v. 28, n. 9, p. 1137 (Sept. 1956).

25. Clifford, D. A., "Total Oxygen Demand - A New Instrumental Method," Proc. 24th Annual Scientific Meeting, Midland Section, Am. Chem. Soc., Midland, Michigan (1967).

26. Cochran, L. G. and Bess, F. D., "Waste Monitoring by Gas Chromatography," J. WPCF, v. 38, n. 12, p. 2002 (Dec. 1966).

27. Cooper, W. C. and Tabershaw, I. R., "Biologic Effects of Nitrogen Dixoide in Relation to Air Quality Standards," Arch. Environ. Health, v. 12, n. 3, p. 522 (1966).

28. Dickerson, B. W., Campbell, C. J. and Stankard, M., "Further Operating Experiences on Biological Purification of Formaldehyde Wastes," Proc. 9th Ind. Waste Conf., Purdue Univ., p. 331 (1954).

29. Dougan, L. D. and Bell, J. D., "Waste Disposal at a Synthetic Rubber Plant," Sew. and Ind. Wastes, v. 23, n. 2, p. 181 (1951).

30. DuBois, K. P. and Geiling, E. M. K., Textbook on Toxicology, Oxford University Press, New York, N. Y. (1959).

31. Eckenfelder, W. W., Jr., Lecture Series Prepared for Manufacturing Chemists Assoc., The Univ. of Texas, Austin (1967).

32. Eckenfelder, W. W., Jr., Ford, D. L. and Burleson, N. K., Unpublished Rept. (July 1968).

33. Elkin, H. F., "Condensates, Quenches, Wash Waters as Petrochemical Waste Sources," Sew. and Ind. Wastes, v. 31, n. 7, p. 838 (July 1959).

34. Ettinger, M. B., "Proposed Toxicity Screening Procedure for Use in Protecting Drinking Water Quality," J. AWWA, v. 52, n. 6, p. 689 (June 1960).

35. Farrett, J. T., "Toxicity Considerations in Pollution Control," Ind. Wastes, v. 2, n. 1, p. 17 (Jan. 1957).

36. Ford, D. L. and Eckenfelder, W. W., Jr., Unpublished Rept. (March 1968).

37. Ford, D. L. and Gloyna, E. F., Unpublished Rept. (Jan. 1967).

38. Ford, D. L. and Gloyna, E. F., Unpublished Rept. (Feb. 1967).

39. Ford, D. L. and Gloyna, E. F., Unpublished Rept. (May 1967).

40. Ford, D. L. and Gloyna, E. F., Unpublished Rept. (July 1967).

41. Filicky, J. G. and Hassler, J. W., "Effect of Synthetic Detergent Pollution," J. AWWA, v. 42, n. 1, p. 17 (Jan. 1950).

42. Garrett, J. T., "Toxicity Considerations in Pollution Control," Ind. Waste, v. 2, n. 1, p. 17 (Jan. 1957).

43. Gaufin, A. R., "Bioassays to Determine the Toxicity of Pesticides to Aquatic Invertebrates," Proc. 15th Ind. Waste Conf., Purdue Univ., p. 94 (1960).

44. Gloyna, E. F. and Burleson, N. K., Unpublished Rept. (March 1968).

45. Gloyna, E. F. and Malina, J. F., Jr., "Petrochemical Wastes Effect on Water," Ind. Water & Wastes, pt. 1, Sept.-Oct. 1962, pt. 2, Nov.-Dec. 1962, pt. 3, Jan.-Feb. 1963, pt. 4, March-April 1963.

46. Haines, R. M., et. al., Annals of the New York Academy of Sciences, v. 58, p. 158 (March 1954).

47. Henderson, C., Pickering, Q. H. and Lemke, A. E., "The Effect of Some Organic Cyanides (Nitriles) on Fish," Proc. 14th Ind. Waste Conf., Purdue Univ., p. 120 (1960).

48. Hoak, R. D., "Recovery and Identification of Organics in Water," Advances in Water Pollution Research - v. 1, Macmillan, New York, N. Y., p. 163 (1964).

49. Hoak, R. D., "The Causes of Tastes and Odors in Drinking Water," Proc. 11th Ind. Waste Conf., Purdue Univ., P. 229 (1956).

50. Huang, J. C. and Gloyna, E. F., "Effects of Toxic Organics on Photosynthetic Reoxygenation," Center for Research in Water Resources Rept. No. 20, The Univ. of Texas, Austin (1967).

51. Huekelekian, H. and Rand, M. C., "Biochemical Oxygen Demand of Pure Organic Compounds," Sew. & Ind. Waste J., v. 27, p. 1040 (1955).

52. Hueper, W. C., "Cancer Hazards from Natural and Artificial Water Pollutants," Proc. Conf. on Physiol Aspects of Water Quality, USPHS, Washington, D. C., p. 181 (1960).

53. Hutner, S. H., Baker, N., Arronson, A. and Zahalsky, A. C., "Bacteria-Protozoa as Indicators in Purifying Water," Biological Problems in Water Pollution - Third Seminar 1962, R. A. Taft San. Engr. Center, Cincinnate, Ohio, p. 45 (1965).

54. Hynes, H. B. N., "A Survey of Water Pollution Problems," Ecology and the Ind. Society, Goodman, G. T., Edward, R. W. and Lambert, J. M., eds. Blackwell Scientific Publications, Oxford, p. 49 (1965).

55. Ishio, S., "Behavior of Fish Exposed to Toxic Substances," Advances in Water Pollution Research, 2nd Conference, Vol. I, p. 19 (1965).

56. Jones, J. R. E., Fish and River Pollution, Butterworth and Co. Ltd., Washington, D. C., 203 pp. (1964).

57. Kinney, J. E., "Evaluating the Taste and Odor Control Problem," J. AWWA, v. 52, n. 4, p. 505 (April 1960a).

58. Kinney, J. E., "Fusing the Phenol Frenzy," Proc. 15th Ind. Waste Conf., Purdue Univ., p. 29 (1960b).

59. Klein, L., River Pollution II. Causes and Effects, Butterworth and Co. Ltd., London (1962).

60. Kneese, A. V., Water Pollution - Economic Aspects and Research Needs, Resources for the Future, Inc., Washington, D. C. (1962).

61. Krombach, H. and Barthel, J., "Investigations of a Small Watercourse Accidently Polluted by Phenol Compounds," Advances in Water Pollution Research, Vol. I, Macmillan Co., New York, N. Y., p. 191 (1964).

62. Lammering, M. W. and Burbank, N. C., "The Toxicity of Phenol, o-Chlorophenol, and o-Nitrophenol to Bluegill Sunfish," Proc. 15th Ind. Waste Conf., Purdue Univ., p. 541 (1960).

63. Lively, L., Rosen, A. A., and Mashni, C. I., "Identification of Petroleum Products in Water," Proc. 20th Ind. Waste Conf., Purdue Univ., v. 49, n. 4, p. 657 (1965).

64. Martin, J. M., Orr, C. R., Kincannon, C. B., and Bishop, J. L., "Ultraviolet Determination of Phenols," J. WPCF, v. 39, n. 1, p. 21 (Jan. 1967).

65. Mellon, M. G., "Detection and Analysis of Chemicals in Water I. Inorganic Constituents," Proc. Conf. on Physiol. Aspects of Water Quality, U S P H S , Washington, D. C., v. 27 (1960).

66. Mencher, M. R., "Minimizing Waste in the Petrochemical Industry," Chemical Engineering Progress, v. 63, n. 10, p. 80 (1967).

67. Middleton, F. M., Grant, W. and Rosen, A. A., "Drinking Water Taste and Odor," Ind. & Engr. Chemistry, v. 48, n. 2, p. 268 (Feb. 1956).

68. Middleton, F. M. and Lichtenberg, J. J., "Measurements of Organic Contaminants in the Nation's River," Ind. and Engr. Chemistry, v. 52, p. 99A (June 1960).

69. Nemerow, N. L., Theories and Practices of Industrial Waste Treatment, Addison-Wesley Pub. Co., Inc., Reading, Mass. (1963).

70. Polange, R. C., "Mississippi River Water Quality," Southwest Water Works J., v. 42, p. 23 (Aug. 1960).

71. Paynter, O. E., "Chronic Toxicity of Dodecylbenzene Sodium Sulfonate," Proc. Conf. on Physiol. Aspects of Water Quality, USPHS, Washington, D. C., p. 175 (1960).

72. Phelps, E.B., Stream Sanitation, John Wiley and Sons, Inc., New York, N. Y. (1944).

73. Pickering, Q. H. and Henderson, C., "Acute Toxicity of Some Important Petrochemicals to Fish," J. WPCF, v. 38, n. 9, p. 1419 (Sept. 1966).

74. Remy, E. D. and Lauria, D. T., "Disposal of Nylon Wastes," Proc. 13th Ind. Waste Conf., Purdue Univ., p. 596 (1958).

75. Rosen, A. A., "Recent Developments in Sensory Testing," J. AWWA, v. 58, n. 6, p. 699 (June 1966).

76. Ruchhoft, C. C., et. al., "Waste Disposal in Petroleum Industry," Ind. & Engr. Chemistry, v. 46, n. 2, p. 283 (Feb. 1954).

77. Silvey, J. K. G., et. al., "Actinomycetes and Common Tastes and Odors," J. AWWA, v. 42, n. 11, p. 1018 (Nov. 1950).

78. Skold, R. V. and Wilkes, J. R., "Monobed Operation with a Problem Water," Ind. & Engr. Chemistry, v. 47, p. 90 (1955).

79. Sugar, J. W. and Conway, R. A., "Gas-Liquid Chromatography Techniques for Petrochemical Wastes," J. WPCF, v. 40, n. 9, p. 1622 (Sept. 1968).

80. Tarzwell, C. M., et. al., Biological Problems in Water Pollution, USPHS Publication No. 999-WP-25, Cincinnati, Ohio (1965).

81. Taylor, E. F., et. al., "Orlon Manufacturing Wastes Treatment," J. WPCF, v. 33, p. 1067 (Oct. 1961).

82. Teal, J. L, "The Control of Waste Through Fish Taste," American Chem. Soc., Natl. Meeting (1959).

83. Teasley, J. I., "Identification of Cholinestrase-Inhibiting Compound from Industrial Effluent," Environ. Sci. and Tech., v. 1, n. 5, p. 411 (May 1967).

84. Thirumurthi, D. and Gloyna, E. F., "Relative Toxicity of Organics to Chlorella pyrenoidosa," Center for Research in Water Resources Rept. No. 4, The Univ. of Texas, Austin (1965).

85. Timmermans, J., "Odour and Chemical Constitution," Nature (Brit.), v. 174, p. 235 (1954).

86. Todd, D. K., Ground Water Hydrology, John Wiley and Sons, Inc., New York, N. Y., p. 185 (1959).

87. Turnbull, H., Demann, J. G. and Weston, R. F., "Toxicity of Various Refinery Materials to Fresh Water Fish," Ind. & Chemistry, v. 46, p. 325 (1954).

88. Wallen, J. E., Greer, W. C. and Lasater, R., "Toxicity to Gambusia affinis of Certain Pure Chemicals in Turbid Waters," Sew. and Ind. Wastes, v. 29, n. 6, p. 695 (June 1957).

89. Weintraub, R. L., Rocky Mountain Arsenal Waste Status Rept. 25 (May 1959).

90. Willingham, C. A. and Andersen, K. J., "Use of Microorganisms for Detecting Toxic Materials in Water, Part I, Water and Sew. Works, v. 113, n. 12, p. 464 (Dec. 1957).

91. Wilson, I. S., "The Treatment of Chemical Wastes," Waste Treatment, Isaac, P.C.G., ed, Pergamon Press, London, p. 206 (1960).

92. Wright, R. H., et. al., "Odour and Molecular Vibrations III. A New Theory of Olfactory Stimulation," Chem. and Ind. (Brit.) p. 973 (Sept. 1956).

93. Zapp, J. A., Jr., "Minimal Effects of Organic Water Contaminants," Proc. Conf. on Physiol. Aspects of Water Quality, U S P H S Washington, D. C. (1960).

CHAPTER VII

TREATMENT AND CONTROL OF PETROCHEMICAL WASTES

This chapter deals with methods presently used for the control, treatment, and ultimate disposal of petrochemical wastes. The treatment and control processes discussed here are categorized as follows: (a) reduction of waste strength by in-process and in-plant control measures, (b) physical treatment processes, (c) chemical treatment processes, (d) biological treatment processes, and (e) ultimate disposal techniques.

REDUCTION OF WASTE LOADS BY INTERNAL IMPROVEMENTS

An ideal method for controlling petrochemical pollutants is to minimize and control unavoidable losses near the source. Such practice reduces the cost of waste treatment and in many cases provides a valuable economic gain.

Reduction of Raw Material Losses

The losses of raw materials from storage, transport, and processing facilities are an important source of water pollution in the petrochemical industry. For example, Table IV-2 indicates that 0.21 percent of hydrocarbon feedstock can be lost in a carefully controlled plant, but in plants where less extensive control practices are employed, as much as 0.6 percent may be lost (Mencher, 1967). Several improvements can be made by the industry to reduce the magnitude of these losses. The evaporation of light hydrocarbons from storage tanks can be controlled through the use of floating roof tanks and vapor recovery lines in tank vents and purge lines used for process start-up and shut-down can be connected to vapor recovery systems (Mencher, 1967). The hydrocarbon losses from vacuum jets can be reduced by installing refrigerated condensors ahead of the jets (Hyde, 1965) or by connecting the jet exhaust to vapor recovery systems (Mencher, 1967).

Pipeline systems should be used to transfer raw materials whenever feasible in order to minimize transfer losses. Many petrochemical industries minimize transport hydrocarbon losses by either having subsidiary companies which supply raw materials or by producing their own. Probably the most important source of hydrocarbon raw material loss is from malfunctioning equipment lines, leakages, pump gland leakage, etc. These losses can be corrected only by careful and persistent in-plant control.

Recovery of Usable Reaction Products

By-products represent a significant pollutional fraction of petrochemical wastewaters and in many cases, by-product recovery from the process wastes is justified not only in terms of producing a product, but also in reducing the pollutional load. The recovery of sulfur from crude oils, for example, minimizes the sulfide and mercaptan pollution. Many petroleum feedstocks contain large amounts of these sulfur compounds which must be removed to prevent the poisoning of process catalysts and products, and it is possible to recover sulfur from these hydrocarbon feedstocks by removing hydrogen sulfide in the form of acid gas using hydrodesulfurization. Hydrodesulfurization consists of removing the hydrogen sulfide from a process stream by stripping with steam or water. The hydrogen sulfide then is stripped from the water or condensate as acid gas.

Two methods are currently used to convert hydrogen sulfide to elemental sulfur. The Claus Process and its modifications are the most common methods or recovering sulfur from petroleum feedstocks. Basically this process consists of forming sulfur dioxide by controlled partial combustion of hydrogen sulfide with air, followed by a reaction between sulfur dioxide and the remaining hydrogen sulfide to yield elemental sulfur (Anon., Oil & Gas J., 1964). The second technique is a catalytic combustion process used for acid gases with a hydrogen sulfide concentration too low to support non-catalytic combustion (Anon., HydrocProc., 1967). In 1963, the production of sulfur in the United States from acid gases totaled nearly one million tons. This procedure is usually an economical way of eliminating an important source of pollutant. In another example, a refinery in Germany hydrodesulfurizes the distillate from the crude-oil splitter and converts the hydrogen sulfide to sulfur (Anon., Oil & Gas J., 1960), eliminating the need for sweetning, acid treatment, and caustic washing.

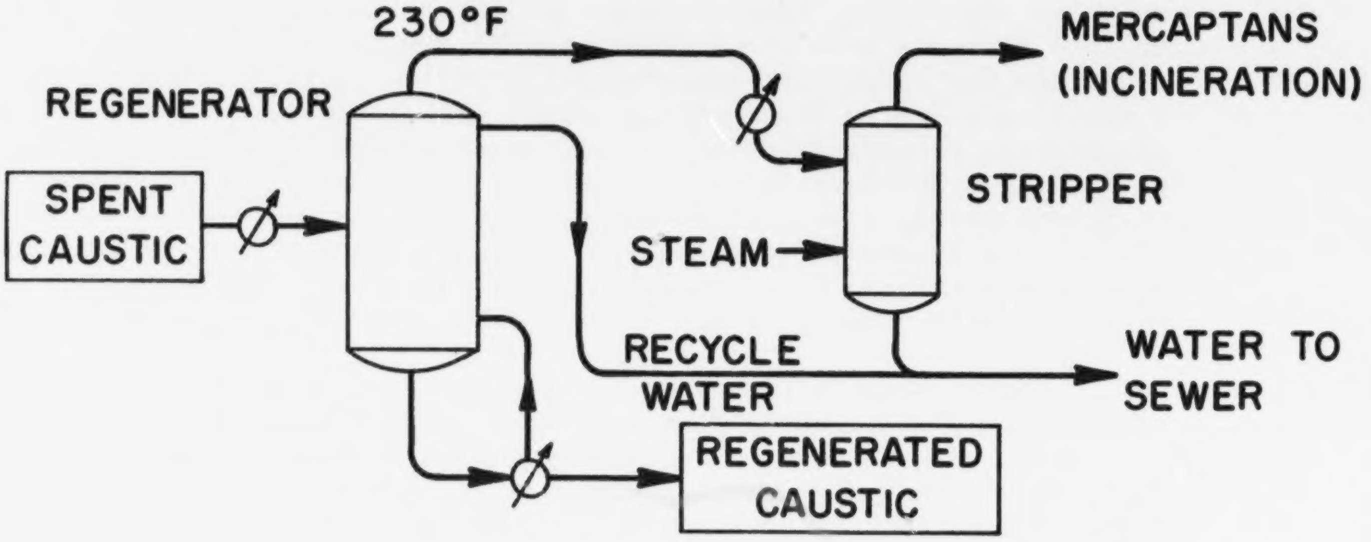
Other sources of usable materials found in petrochemical wastes are the catalyst complex metals and the tars from catalytic processes. For example, a chemical company has sold a copper-containing tar to a smelter, which subsequently recovers the copper (Garrett, 1959). Other metals such as nickel may also be present in evaluating quantities in tars and metal complexes. Chemical recovery companies also have reclaimed useful organic materials from tars. Usually the recovery of materials from these tars does not result in a direct profit to the petrochemical plant, but it may prove economically justified in terms of a reduced pollutional discharge.

Alkaline wastes from caustic washes are most significant and there are several methods available utilizing these caustic wastes which may prove more feasible than attempting to treat and discharge them. Some spent caustic solutions containing sulfides, phenolates, cresolates, and carbonates are marketable (McRae, 1959). Spent caustics containing large amounts of phenols and cresols can be sold to processors who separate and purify the cresylic acid fractions for commercial use (Beychok, 1967). Petroleum-based cresylic acids have become an important marketable product and sodium sulfide can be separated from spent caustics high in sulfides and can be sold. The spent caustic is often enriched in sulfides by using it to absorb hydrogen sulfide present in sour gas streams (Beychok, 1967). The recovery and marketing of spent caustics is probably the most economical and desirable method for eliminating these wastes is a favorable product demand is prevalent.

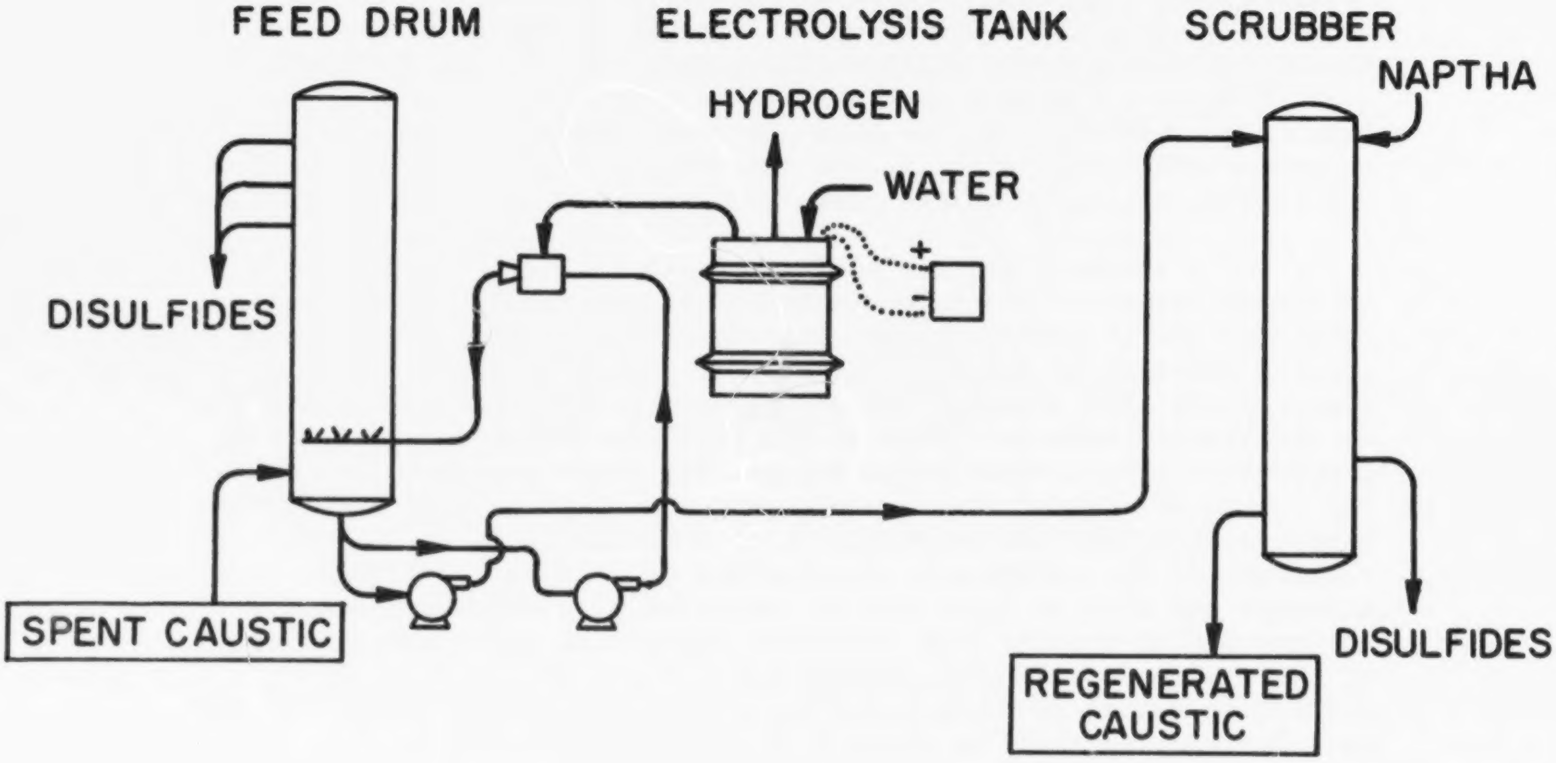
Spent caustics can also be regenerated by steam hydrolysis, electrolysis, air regeneration, and the use of slaked lime (McRae, 1959) for reuse in caustic washing processes. While this method does not eliminate the problem of spent caustic disposal, it does minimize the quantity of spent caustic wastes produced. Steam hydrolysis is the most commonly used regeneration process (McRae, 1959) and as much as 90 percent of the caustic soda can be restored by steam hydrolysis and air oxidation processes. Spent caustics containing phenolic compounds cannot be recovered using these processes, since phenolic compounds with sodium functional groups cannot be renegerated by steam hydrolysis. Phenolics also interfere with the oxidation process. Mercaptans but not sulfides can be renovated; so a gradual buildup of sulfide occurs in the recovered caustic, necessitating the eventual disposal of the caustic waste. Electrical regeneration utilizes the oxygen formed from the electrolysis of water to refresh the caustic and convert the sulfur to marketable polysulfides. As with the other two processes, phenolic compounds will interfere with the renewal process. The two methods for caustic regeneration are steam and electrical (Figure VII-1).

The recovery and recycle of process effluents containing unreacted raw materials allows substantial savings in raw material purchases and is common to most petrochemical processes in which the process reaction is incomplete. Many of the secondary reaction by-products are also valuable for use within the petrochemical plant or as marketable products. Some of the possible uses for by-products produced in three common petrochemical processes are shown in Table VII-1. An example of the in-plant use of a by-product is the use of hydrogen chloride from hydrochlorination processes as one of the reactants in the additional chlorination of olefins. Hydrogen chloride can also be recovered and marketed as a salable product. The removal of phenols from effluents containing recoverable quantities of these compounds is often economical. For example, the Emscher River Association in Germany recovers large quantities of phenol from wastewater at a profit of about $300,000 per year (Clarke, 1962).

The recovery and reuse of oils is extremely common in the petrochemical industry. Recoverable oils are reprocessed while those which are uneconomical to purify are used as a fuel source. Solvent recovery is also often practiced, especially when the high costs of


230°F
REGENERATOR
MERCAPTANS (INCINERATION)
SPENT CAUSTIC
STRIPPER
STEAM
RECYCLE WATER
WATER TO SEWER
REGENERATED CAUSTIC

STEAM REGENERATION


FEED DRUM
ELECTROLYSIS TANK
SCRUBBER
NAPTHA
HYDROGEN
WATER
+
-
DISULFIDES
SPENT CAUSTIC
REGENERATED CAUSTIC
DISULFIDES

ELECTRICAL REGENERATION

FIGURE VII-1

CAUSTIC REGENERATION PROCESSES

(Reference 81)

TABLE VII-1

USABLE SIDE-PRODUCTS FROM SOME TYPICAL PETROCHEMICAL PROCESSES

(Reference 99)

Primary Product	Side-Products	Use
Butadiene:	Residue Gas (Hydrogen, methane, ethane ,carbon dioxide)	Fuel
	Propane and Propylene	Feedstock for Ethylene, Alkylation
	Butane and Butenes	Recycle for Butadiene Manufacture; Feedstock for Alkylation
	Aromatic Oils	Resin or Plastic Manufacture
Ethylene:	Residue Gas (Hydrogen, Methane)	Fuel
	Acetylene	Fuel for Welding Feedstock for Several Petrochemical Processes
	Ethane	Recycle for Ethylene Manufacture; Cracking Feedstock; Fuel
	Propane and Propylene	Propane Recycle for Ethylene Manufacture; Feedstocks for Several Petrochemical Processes (Alcohol, Alkylation, Polypropylene, etc.)
	Butane and Butylene	Feedstock for Synthetic Rubber Aviation Gas; Recycle to Cracking Process
	Aromatic Concentrate	Resin and Plastic Manufacture
	Heavy Oils and Tars	Refinery Charge Stock Fuel

TABLE VII-1 (Continued)

USABLE SIDE-PRODUCTS FROM SOME
TYPICAL PETROCHEMICAL PROCESSES

Primary Product	Side-Products	Use
Ammonia:	Carbon Dioxide	Dry Ice, Bottled CO_2 Fuel Methanol Manufacture
	Helium	Lifting Gas Inert Gas
	Argon	Inert Gas

solvents are considered. A comprehensive list of all of the possibilities of waste component reuse would be virtually limitless. Ingenuity often finds a use for a seemingly unusable waste or waste component. For example, a styrene plant had an oily sludge which was difficult to dispose of because of its physical and chemical properties (Martin and Rostenbach, 1953). It was found that this sludge could be separated into two fractions, an oil which could be used for boiler fuel and an aqueous aluminum chloride solution which was used effectively as a weed killer.

Process Modifications

Process modifications incorporated into the design and operation of petrochemical processing units can often lead to reductions in the pollutional load from the plant. These modifications can be classed as follows: (a) process selection, (b) prevention of product and chemical losses, and (c) modified operating conditions (Anon., API, Vol. III., 1958).

The problems of waste control should be initially considered during the development and design of petrochemical processes, since they can often be an important factor in the economics of operation. Pilot plants used in the design of petrochemical processes can be sampled to estimate the process losses and the type of pollutants which will be discharged from the prototype unit (Anon., API, Vol. III., 1958). Analyses of these samples will indicate possible process modifications which can be implemented to reduce the pollutional load.

The incorporation of spent caustic regeneration schemes in process and plant design is an example of process selection used to reduce the waste load. The substitution of continuous processes for batch processes also tends to eliminate peak discharges of wastes and to reduce the cost of treatment required for the waste (Anon., API, Vol. III.,1958). Treatment facilities designed to absorb the effects of shock discharges of wastes through equalization basins or overdesigned tanks are considerably more expensive than those which are designed to treat a waste of relatively constant consumption.

The use of downgraded chemicals in processes which do not require high-quality reactants can facilitate both process and waste control (Anon., API, Vol. IV., 1958). This type of design utilizes the waste effluents from one process as reactants in another. In the ideal scheme, a chemical could be carried through several processes, each using a slightly lower quality reactant. Caustic washes are often so used in refining operations. For example, caustic washes used to treat light hydrocarbons can later be used as make-up caustic for gasoline treating (Anon., API, Vol. IV.,1958).

An example of how waste treatment costs can enter into both process design and chemical loss control is shown in the example below:

	Redesign of extraction columns	Biological waste treatment plant
Capital Investment	$300,000	$300,000
Yearly Operating Cost:		
Labor, supplies, etc.	1,000 (addtl.)	73,000
Recovered organics	-36,000 (savings)	0
Net cost	-35,000 (savings)	73,000
Total difference	$108,000	

Such chemical recovery units are often designed so that losses from the units are less than those which should be allowed based solely on the economics of recovery (Anon., API, Vol. III.,1958).

The hydrocarbon losses associated with the use of barometric condensors are an important source of pollution in petrochemical processes (Gloyna and Malina, 1962). The use of shell and tube heat exchangers rather than barometric condensors can significantly reduce this source of pollution (Ruggles, 1959). Process sampling taps connected directly to sewers are a source of pollution which can be avoided by returning drainage to the process unit rather than the sewer. Pollution caused by open-bottom steam stills can be controlled by the installation of calandrias (Hyde, 1965). Distillation of waste streams can also be used to eliminate the loss of volatile materials (Martin, and Rostenbach, 1953). Furfural, for example, is recovered by azeotropic distillation, eliminating this compound from wastewaters while producing a valuable solvent for use in extraction processes. One example of waste control by process modification has been the elimination of oil emulsion losses from barometric condensors on pipe still (Anon., API, Vol. III.,1958). By rearranging the interior of the pipe still to reduce friction losses through the trays and by lowering the temperature in the still, losses were reduced to one-sixth of their original quantity.

Water Reuse

Water reuse is often one of the most effective and economical means of reducing the waste discharges from a petrochemical plant. In addition to reducing water costs and waste treatment costs, water reuse increases the flexibility for plant expansion. Small quantities of concentrated wastes produced by reuse are easier to handle than large quantities of dilute wastes, and the plant enjoys more freedom from upstream pollution (Clarke, 1962).

The recycle of cooling water is already common in the petrochemical industry, and the practice will become more popular in the future. Potential applications of water reuse include the utilization of poorer quality cooling water and boiler water and the reuse of contaminated steams in stripping operations and in boilers (Rice, 1966). The advent of deposit control agents and the application of corrosion resistant metal alloys in cooling coils and boilers has greatly increased the concentrations allowed for cooling and boiler waters.

Water use systems are classified as multiple recycle and cascade but most frequently combinations of these schemes are utilized (Clarke, 1962). Multiple recycle involves the use of a number of water systems carrying various qualities of cooling or process waters. These systems are segregated and may have self-contained treating systems, but usually operate with continuous blow-down and make-up to keep the water at the desired quality. In cascade systems which integrate process and cooling waters rather than segregate them (Clarke, 1962), high quality water flows first to the process requiring the cleanest water and subsequently to successive processes where poorer water qualities can be tolerated.

Steam used for the stripping and quenching of process streams is an important source of waste in the petrochemical industry. Various treatment methods are available to reclaim these condensates for reuse as will be discussed in detail later. One use for condensates which requires little pretreatment is as a feedwater to waste heat steam generators (Rice, 1966). Condensates with high sulfide contents can be oxidized to convert the sulfides to sulfate and then used to generate low-quality stripping steam. Another condensate reuse scheme has been described (Mencher, 1967) in which phenolic condensate from an olefin unit is washed with the fresh hydrocarbon feed stream thus removing the phenol from the condensate. Other volatile hydrocarbons are then steam stripped from the condensate and reused to generate additional steam. Many additional schemes for condensate reuse can be developed, depending on water quality requirements for a particular use.

A potential source of water for reuse in the petrochemical plant is in the main boilers. These boilers usually operate with superheated steam and can be damaged by solids deposition when poor quality water is used (Rice, 1966). However, boilers can often tolerate high dissolved solids concentrations, depending on the type of dissolved matter and the boiler design. The use of sequestering agents to prevent deposition has also contributed towards reducing problems associated with oils in boiler waters (Rice, 1966). If chelating agents are present, oils are distilled or leave the boiler with the blow-down. If lower quality waters could be used in boilers, the boilers could in effect act as concentrating units for refractory materials (Rice, 1966).

In-Plant Control

Operational control is one of the most important facets of pollution abatement. The organic waste load (as BOD) at a West Virginia chemical plant was reduced an estimated 40,000 lb/day merely by instituting proper control techniques. In-plant operational control includes (a) maintenance of pipes, valves, fittings, pump seals, etc., to prevent leaks; (b) education of all plant personnel as to the effects of accidental and careless losses of materials; (c) changes in some operational procedures; and (d) a highly developed monitoring system to detect the sources and occurrences of pollutants within the plant.

A continuous monitoring program for important plant sewers can prove invaluable in locating malfunctioning process units and leaks. For example, butanol escaping from a distillation unit was discovered in a wastewater which was continuously monitored using gas chromatography techniques (Cochran and Bess, 1966). The unit was subsequently repaired, significantly reducing a source of pollution as well as the loss of a valuable chemical product.

Waste Stream Segregation

Segregation systems used by the petrochemical industry vary widely depending upon reuse requirements, effluent quality requirements, and possible undesirable effects which might occur if incompatible effluents are mixed. Three main segregated collection systems are normally used (Anon., API, Vol. III.,1958):

a) area drains which carry unpolluted cooling water and storm water runoff from uncontaminated areas;

b) a contaminated water system which contains process waters, polluted cooling waters, and storm water runoff from contaminated areas; and

c) a sanitary sewage system to collect plant domestic wastes.

Many petrochemical plants segregate wastewaters to an even greater extent. For example, oily process wastewaters are frequently segregated from non-oily wastewaters to facilitate oil removal through separators.

Segregation of many process streams may be necessary due to the incompatability of certain waste components. Wastes containing cyanides, for example, must be separated from acidic effluents to prevent the release of gaseous hydrogen cyanide. Wastes with high solids concentrations are usually segregated from oily streams since suspended solids tend to increase the oil concentrations in oil separation effluents. Suspended solids can also interfere with the recovery of oils by increasing the solids contents of separator skimmings (Anon., API, Vol. III., 1958).

Most water reuse schemes also require additional waste stream segregation and the design of the segregation system will depend upon the type of water reuse being employed at the individual plant. If biological treatment is used to stabilize petrochemical wastes, the sanitary sewage is usually added to it prior to treatment as a source of biological nutrients; but many regulatory agencies require effluent chlorination when sewage is added, making such a combination unfeasible. The unpolluted cooling and storm waters which constitute the largest volume of water discharged by the petrochemical industry normally do not require treatment and are discharged directly to the receiving body of water or effluent waterway.

PHYSICAL TREATMENT PROCESSES

The types of physical treatment processes most commonly used in the treatment of petrochemical wastes include gravity separation, flotation, stripping processes, adsorption, extraction, and combustion.

Gravity Separation

Gravity separation includes the removal of materials less dense than water, such as oils and air-entrained particulates, by flotation and the removal of suspended materials which are more dense than water by sedimentation. Sedimentation and flotation techniques commonly employ chemical conditioners to enhance the separation. These separation aids will be discussed in a subsequent section.

Oil Separation - The separation of oil by gravity is a common unit process in petrochemical plants. Many of the wastewaters from petrochemical operations contain significant quantities of free and emulsified oil-like materials which must be removed before subsequent treatment can be obtained. Some of the petrochemical processes which release sufficient amounts of oil are listed in Table VII-2. In general free oils are easier to remove if their concentration is high, indicating that treatment of oily water streams prior to dilution with non-oily waste streams will provide for more efficient oil separation. Slop oils recovered by the separation process can be cleaned and reused in various processing operations and as fuel oils for generating steam (Shannon, 1964; Martin and Rostenbach, 1953).

TABLE VII-2

SPECIFIC APPLICATIONS OF OIL SEPARATORS IN THE PETROCHEMICAL INDUSTRY

Products	Waste Stream or Process Effluent Requiring Separation	Ref
Acrylonitrile and Lineal Alkylate Sulfonate Detergents	Process Effluents	102
Butadiene Rubber	Process Area Feed Preparation Area, Recovery Area Tank Farm	77
Copolymer (GR-S) Rubber	Polymerization Process Area Total Plant Effluent Tank Farm	77
Cracking for Ethylene, Propylene and Butadiene	Excess Quench Water	104
Hydrocarbons in General (General Refining Processes	Distillation Thermal and Catalytic Cracking Reforming Alkylation Isomerization	103
Hydrocarbons from Cracking of Light Crudes	Condensates	102
General Petrochemicals	Acetaldehyde Acetone Acetylene Derivatives C_8 Aromatics Benzene Detergents Diethyl Ether Aromatic Distillates Ethyl Benzene Ethyl Ether	10

TABLE VII-2 (Continued)

SPECIFIC APPLICATIONS OF OIL SEPARATORS IN THE PETROCHEMICAL INDUSTRY

Products	Waste Stream or Process Effluent Requiring Separation	Ref
General Petrochemicals (Cont.)	Flux Oil Gasolines Kerosines Naphtha Polybutenes Resins Tars Toluene Urea Xylene	
Styrene Rubber	Total Plant Effluent	77

For example, at a butadiene plant in California, 40 barrels of oil per day were recovered and reused (Martin and Rostenbach, 1953).

Several basic designs of oil separators have been successfully implemented into the petroleum industry. Probably the most commonly employed separator design is that presented in the American Petroleum Institute's (API) Manual on the Disposal of Refinery Wastes (1953). The API has performed extensive theoretical and experimental research on separator design with the results summarized in this manual (Anon., API, Vol. I., 1953). Other types of oil separators used by the petrochemical industry are circular separators which when properly designed can also be used as sedimentation tanks (Word, et. al.); skim and surge tanks used to equalize the strength and flow of wastewater are very effective oil removal facilities (Huber, 1967); and parallel-plate oil separators (Huber, 1967; Beychok, 1967; Brunsmann, et. al., 1962). Such separators have given higher oil removal efficiencies than conventional separators, probably because of the shorter distance the oil must travel to the collecting surface (Eckenfelder, 1966). Reported efficiencies of some oil-separators operated by the petroleum industry are given in Table VII-3. High oil concentrations are removed with greater efficiency than low oil concentrations since the lower limit of oil in the effluent from a separator is usually 20 to 50 mg/1. Some reduction in chemical oxygen demand (COD) can be anticipated because of the removal of oils and tars, but little or no reduction in biochemical oxygen demand (BOD) can be expected. One oil separator reported in Table VII-3 indicated a 55 percent removal of phenols, but it is doubtful that such a high phenol removal can be maintained by physical separation. It is possible that the oils in this separator acted as solvents, extracting the phenols from the wastewater.

The principal factors which affect the design of oil-water separators are

a) the specific gravity of the oil,

b) the specific gravity of the wastewater,

c) the temperature of the wastewater stream,

d) the presence or absence of emulsions, and

e) the suspended solids concentration.

The specific gravities of the oil and water determine the separation rate while these specific gravities are in turn related to temperature. These factors determine the allowable overflow rate from the oil separator. Graphical solutions of oil-water separation rates which can be used for separator design have been prepared (Reinbald, 1960).

TABLE VII-3

TYPICAL EFFICIENCIES OF OIL SEPARATION UNITS.

Oil Content		Oil Removed (%)	Type	COD Removed (%)	BOD Removed (%)	Phenol Removed (%)	Ref
Influent (mg/1)	Effluent (mg/1)						
7,000-8,000	125	98-99+	Circular	-	-	-	112
3,200	10-50	98-99+	Impounding	0	-	-	90
400-200	10-40	90-95	Parallel Plate	-	-	-	66
220	49	78	API*	45	-	55	13
108	20	81.5	Circular	-	-	-	117
108	50	54	Circular	16	0	0	13
90-98	40-44	55	API	-	-	-	13
50-100	20-40	60	API	-	-	-	13
42	20	52	API	-	-	-	13

* API - American Petroleum Institute Standard Design

Emulsions present the biggest problem of oil-water separation in the petroleum industry of which the most common type is the oil-in-water emulsion where minute droplets of oil are dispersed throughout the liquid medium (Anon., API, Vol. I, 1953). The usual concentrations of oil found in wastewaters from the petrochemical industry would cause these droplets to coalesce and separate from the water phase, however the emulsions are stabilized by the presence of a third compound, classified as an emulsifying agent. Some of the compounds commonly found in petrochemical wastes which produce this surface-active effect include the sulfonic acids, the naphthenic acids and the fatty acids, as well as their sodium and potassium salts. In an alkaline medium calcium and magnesium salts form finely divided suspended solids which stabilize emulsions (Phillips, 1954). Also, other forms of suspended solids sometimes tend to stabilize emulsions. Sources of oil emulsions within a petrochemical plant include (a) crude oil desalting water, (b) condensates from distilling operations, (c) wash waters which follow caustic or acid chemical treating operations, (d) cooling waters from barometric or other direct-contact condensors, (e) detergent manufacturing processes, and (f) equipment cleaning operations (Anon., API, Vol. I, 1953).

In order to separate these oils from the wastewater, the emulsion must first be broken by using both physical and chemical methods. The appropriate procedures for effectively treating an emulsified oil waste must be determined by a laboratory investigation. The application of heat is probably one of the more effective methods used for de-emulsification of a waste (Anon., API, Vol. I, 1953). Heat decreases the viscosity of the oil phase, promotes the settling of free water, and increases the vapor pressure of the water, rupturing the film around the oil droplet (Anon., API, Vol. I, 1953). Pressure and heat systems can be used, and distillation methods, in lieu of the heat requirement, are also effective. Additionally the surface active materials which act as emulsifying agents are left in the still residue and can be disposed of separately.

Filtration and electrical methods have also been used to treat emulsions. Filtration will be discussed separately in the physical treatment section. Electrical methods involve the use of a strong electrical field causing the water phase to coalesce and separate from the oil by gravity (Anon., API, Vol. I, 1953). Several of these emulsion-breaking methods are often combined to achieve the desired results. It should be noted that total oils in excess of 50 mg/l generally may have a deleterious effect on secondary biological processes, and oil separation facilities in such system produce an effluent with less than this concentration.

Sedimentation - Sedimentation processes are employed in pre- or primary treatment of petrochemical wastes with high suspended solids concentrations, in secondary clarification, and as a sludge thickening device. Petrochemical wastewaters high in colloidal material must be chemically treated before adequate separation by sedimentation can be obtained. Primary settling also has been used to remove lead from wastes from tetraethyl lead manufacture (Gill, et. al., 1960).

Operational data from the sedimentation of various petrochemical wastes are given in Table VII-4. These data indicate that conventional removal efficiencies of suspended solids can be obtained.

The removal of solids and oils from petrochemical wastewaters and the concentration of sludges can often be accomplished using a flotation process. When the mixture of suspended material and air-saturated water is exposed to atmospheric pressure in the flotation tank, minute air bubbles are released from solution and carry the suspended materials to the top of the tank. In this scheme air is dissolved under pressures of 30 to 60 psig in the raw waste or in a portion of the clarified effluent. The efficiency of this process is shown in Table VII-5.

The recycle system, where air is injected into a portion of the effluent, has been successfully used for treating petroleum and petrochemical wastes. In most cases, chemical aids must be added to the waste to enhance the solids-liquid separation and gravity oil separators precede the flotation unit. The high efficiency of the flotation units in terms of COD removal for petroleum waste is noted in Table VII-5 because many of the organics are associated with the suspended material. However, flotation unit efficiency is expected to be lower when considering petrochemical wastewaters in which more of the organic contaminants are in soluble form.

The flotation design ranges for petrochemical wastes are (a) pressure 30-60 psig, (b) detention time in the flotation tank of 15-30 minutes, and (c) an overflow rate of two to three gal/min/ft^2. A recycle system pressurizing clarified effluent is normally used and the depth of the flotation tank will be six to eight feet, depending upon the rise rate of the suspended material. Provisions must be made for the disposal of the flotation tank skimmings, the most common methods being incineration and landfill. One of the big advantages of flotation over sedimentation is the shorter detention time required to clarify a waste by flotation, resulting in a unit considerably smaller in size.

These separation processes will only partially treat a petrochemical waste; thus, the effluents from most plants may still be objectionable from a pollutional point of view. If the waste stream being treated is low in dissolved organic material, then it is possible that only filtration will be required as additional treatment prior to discharge to the environment. This is an exception, however, and most petrochemical wastes have high concentrations of soluble organic compounds requiring additional treatment prior to final discharge.

TABLE VII-4

SEDIMENTATION OF SOME PETROCHEMICAL WASTES

Waste	Suspended Solids			BOD			Remarks	Ref
	Influent (mg/1)	Effluent (mg/1)	Reduc. (%)	Influent (mg/1)	Effluent (mg/1)	Reduc. (%)		
Amines, Amides	30	3	90	150	140	6.7	Neutral, Follows	26
Drugs	-	200	-	-	500	-	-	26
PVC Plastics	500	20-40	92-96	150	60	60	Neut., Coagulation	26
Refinery	100	25	75	125	90	28	Coagulation	117
Refinery, Nat. 2	200	30-50	75-85	-	-	-	Step (1) Neut.	90
Gas Liquids, Chem. Specialties	30-50	5-20	33-90	-	-	-	Step (2) Coagulation	
Resins	8,000	8	99+	130	125	3.8	pH Adjusted	26

TABLE VII-5

PERFORMANCE AND OPERATING CHARACTERISTICS OF FLOTATION UNITS TREATING PETROLEUM WASTES

Removal Efficiencies									
Oil		S. S.		COD					
Infl. ppm (mg/1)	Removal (%)	Infl. (mg/1)	Removal (%)	Infl. (mg/1)	Removal (%)	Pressure (psig)	Overflow rate (gpm/ft^2)	Remarks	Ref
89-244	61-63	-	-	-	-	-	-	-	27
125	64-76	-	-	-	-	-	-	No Chemicals Added	112
41-638	61-95	-	-	-	-	-	-	7 ppm organic polymer added	13
-	Substantial	-	Substantial	100-10,000	70-92	-	-	Phosphates Added, +pH Adjustment.	92
-	94	-	-	-	-	-	-	Recycle, 4 ppm + 4 ppm Activated Silica	27
-	84	-	-	-	-	-	-	Recycle, 4 ppm Alum	27
-	62	-	-	-	-	-	-	Recycle	98
-	85-95	-	70-75	-	65-85	35-55	3.0	Recycle, 25 ppm Alum Added	13

Stripping Processes

Stripping methods are used to remove volatile materials from liquid streams. Stripping is usually used to remove relatively small quantities of volatile pollutants from large volumes of wastewater (Anon., API, Vol. III, 1958). The two types of stripping agents commonly used are steam and inert gas. When steam is used to strip a volatile compound from an aqueous solution, the steam serves both as a source of heat and a diluent to reduce the effective pressure (Anon., API, Vol. III, 1958). The use of an inert gas, such as natural gas, for a stripping agent precludes condensation of volatile compounds stripped from solution. However, the indiscriminant use of inert gases for waste stripping may lead to air pollution problems.

Stripping of hydrogen sulfide and occasionally ammonia from sour waters is probably this method's most common use in the petrochemical industry. The design criteria for sour water strippers is well documented and is outlined comprehensively elsewhere (API, Vol. III, 1958; Beychok, 1967). Most of the stripping methods involve the continuous downward flow of the wastewater through a packed or trayed tower while the stripping gas or steam flows upward removing the desired constituent (Beychok, 1967). The operating characteristics of steam, natural gas, and flue gas, the major stripping agents used to remove hydrogen sulfide and ammonia, are listed in Table VII-6. If the aqueous wastes are acidified with a mineral acid prior to stripping, the ammonia is "fixed" in solution as the ammonium salt of a strong acid and the hydrogen sulfide is released to solution where it can easily be stripped. The temperatures may be as low as 100°F. This method leaves ammonia in the process wastewater, which may be desirable as a nutrient for biological waste treatment processes.

Steam is considered to be the preferred heating and stripping agent for the removal of hydrogen sulfide and ammonia. One advantage of steam is that hydrogen sulfide, which is concentrated in the steam condensate, may be further treated. Flue gases are frequently used because carbon dioxide produces a slightly stronger acid than hydrogen sulfide thus releasing hydrogen sulfide from solution. In this step the ammonia is not released. Additionally, the heat in the flue gas is sufficient to raise the wastewater to stripping temperature without a supplemental heat source. The principal disadvantages of flue gas are larger piping and equipment, corrosion, and the release of hydrogen sulfide to the atmosphere.

Natural gas has also been used as an inert stripping gas to remove hydrogen sulfide from sour wastewaters; however, steam must be used to raise the temperature to at least 230°F (Beychok, 1967).

TABLE VII-6

AVERAGE OPERATING CHARACTERISTICS OF SOUR WATER STRIPPERS

(Reference 12)

Type of Stripper	Flow Rate of Stripping Medium (SCF/gal)	Removal		Temperature	
		H_2S (%)	NH_3 (%)	Tower Feed (°F)	Tower Bottom (°F)
Steam					
w/o acidifying[+]	8-32	96-100	69-95	150-240	230-270
w/ acidifying[**]	4-6	97-100	0	200	230-250
Flue Gas					
w/ steam[*]	12.7	88-98	77-90	235	235
w/o steam[*]	11.9	99	8	135	140
Natural Gas					
w/ acidifying	7.5	98	0	70-100	70-100

[+] Data from Eight Towers

[*] Data from Only One Tower

[**] Data from Two Towers

Steam also has been used as a stripping agent in the removal of other petrochemical waste components. Phenols can be removed from aqueous waste streams by stripping them with steam. Phenol removals of 24 percent and 36 percent were reported when sour waters were stripped for hydrogen sulfide removal with steam and flue gas (Anon., API, Vol. III,1958). Steam stripping of phenolics is applicable when a wastewater is subject to sharp variations in temperature, specific gravity, phenol concentrations, and suspended solids (Heller, et. al., 1957). The condensed phenolic steam is reacted with caustic to remove the phenols. Superheated steam has also been used to strip hydrocarbons from a spent acid catalyst used in methylstyrene production (Federgreen and Weinberger, 1957). This particular stripping process recovers 38 million pounds of sulfuric acid, 9.3 million pounds of toluene, and 62 thousand pounds of mercury per year of operation, which is sufficient to pay for the entire operational cost. Steam has also been used to strip aromatics from the condensate produced during the catalytic dehydrogenation of ethylbenzene for styrene production.

Volatile organic compounds can be stripped from aqueous wastes by using air as the stripping agent. Compressed air purged through a container of wastewater will cause sufficient agitation of the contents to remove large quantities of volatile organic compounds. The stripping rate of a volatile organic compound is a function of temperature, the stripping gas flow rate, and tank geometry (Eckenfelder, et. al., 1956; Gaudy, Englebrecht and Turner, 1961). Both exponential and linear equations have been used to describe the removal of organic compounds from water by air stripping. Laboratory investigations are required to determine how many organic compounds in a particular wastewater can be stripped, and which mathematical relationship defines the particular stripping phenomenen.

Laboratory tests involving stripping of some biodegradable volatile organic compounds indicated that most of the BOD removal in an aeration tank was due to biological action rather than physical stripping (Englebrecht and Ewing, 1962). This investigation indicated that the stripping of biodegradable wastes is not usually significant, even if the organics are quite volatile. If an organic compound is non-biodegradable and volatile, however, air stripping may be a significant mechanism for removing this pollutant from a liquid system. For example, benzene and nitrobenzene,both of which are relatively non-biodegradable, can be effectively air stripped from wastewater. Air stripping systems are often not followed by condensation units because of economic considerations, and the practice of releasing volatile compounds to the atmosphere often creates air pollution problems which limit this treatment technique's efficiency.

Solvent Extraction

Solvent extraction methods utilize the preferential solubility of materials in a selected solvent. Solvent extraction processes are common in petrochemical operations as a separation technique. The criteria for an effective solvent for wastewater treatment include (a) low water solubility, (b) density differential greater than 0.02 between solvent and wastewater, (c) high distribution coefficient for waste component being extracted, (d) low volatility resistance to degradation of heat if distillation is used for regeneration or low solubility in liquid regenerants, and (e) economical to use (Gloyna and Malina, 1962). The equipment used for the extraction of wastewater includes countercurrent towers, mixer-settler units, centrifugal extractors, and occasionally some specially designed equipment (Anon., API, Vol. III, 1958).

Solvent extraction has been used very effectively by the petroleum industry to remove phenols from various process streams. Some of these solvents which have been used to extract phenols from waste streams are tabulated in Table VII-7. Tri-cresyl phosphates are excellent solvents due to their low solubility in water and their high distribution coefficients for phenol, but they are expensive and deteriorate at high distillation temperatures (Anon., API, Vol. III, 1958). Tri-cresyl phosphates and the aliphatic esters might be used when high phenol recoveries are desired for economic reasons, justifying the use of expensive solvents. Most of the other phenol solvents are available within the refinery-petrochemical complex and are considerably cheaper to use in waste treatment operations. The type of extraction equipment required for the use of a particular solvent is also an important economic consideration. For example, centrifugal extractors are much smaller than towers, but have higher capital and operating costs. The electrostatic extractor used in one phenol recovery process also recovers usable oil from wastewater, which helps to make the process economical (Lewis and Martin, 1967). The light cycle oil used as the solvent in this process is used in certain refining processes not requiring phenol removal. This results in much lower regeneration and disposal costs.

Other solvent extraction processes which have been used by the petrochemical industry include the extraction of thiazole-based chemicals from a rubber processing effluent with benzene and the extraction of salicylic and other hydroxy-aromatic acids from a wastewater using methyl-isobutyl-ketone as the solvent (Wilson, 1960). The applicability of solvent extraction methods to a particular compound and waste stream must be investigated in the laboratory and pilot plant. Extraction methods can often be used to significantly reduce the pollutional load in a petrochemical effluent and at the same time provide an economic method of product recovery.

TABLE VII-7

SOLVENTS USED TO EXTRACT PHENOLS FROM WASTEWATER

Solvent	Phenol Influent (mg/l)	Phenol Effluent (mg/l)	Phenol Removal (%)	Remarks	Ref
Aromatics, 75% Paraffins, 25%	200	0.2	99.9	Solvent Regenerated with Caustic-Lab Study	7
Aliphatic Esters	4,000	60	98.5	Regeneration by Distillation	7
Benzene	-	-	90-95	Solvent Regenerated by Distillation	7
Benzene	750	34	95.5	Caustic Regeneration	7
Light Cycle Oil	>300	~ 30	90	Electrostatic Extraction Also Removes Oil from Water at Same Time	71
Light Oil	~ 3,000	~ 35	98.2-99.5	Centrifugal Extraction, Caustic Regeneration	17
Straw Oil Distillates	-	-	95	" "	7
Tricresyl Phosphates	3,000	300-150	90-95	Steam or Caustic Regeneration, Very High Extraction Coefficient	7

Adsorption

Adsorption is the process whereby substances are taken up and become attached to the surface of a solid, by either an electrical, physical, or chemical phenomenon.

Carbon adsorption has been the most successful adsorbent in removing special refractory chemicals from wastewater. Most of the recent work in carbon adsorption has been concerned with the removal of trace organics from treated wastewaters as one of the final steps in complete water renovation. Activated carbon used as a tertiary treatment method for a sewage effluent, for example, has lowered effluent COD values from 40-70 mg/l to 12-20 mg/l (Eckenfelder, 1966).

Examples of refractory materials which are difficult or impossible to remove by conventional biological treatment processes but are removable using adsorption techniques include benzene sulfonates and heterocyclic organic compounds. The actual amount of such a solute adsorbed per unit weight of adsorbent usually increases with increasing concentration of solute. Specific adsorptive capacities of different types of carbons vary for the same solute and this is illustrated by the following data (Morris and Weber, 1966).

Adsorptive Capacities of Activated Carbon:
(0.273 mm particle size @ 30°C)

Carbon	Benzene Sulfonate (mol/g)	2-Dodecyl Benzene Sulfonate (mol/g)
Columbia LC	131	400
Dareo S51	101	420
Fisher	120	344
Norit	92	338
Nuchar C-190	54	316

Phenols, nitriles, and substituted organics can also be adsorbed from wastewaters when they are present in low concentrations. Benzene hexachloride and other chlorinated aromatics have been removed from pesticide manufacturing effluents by using carbon adsorption (Geibler, 1958). These chlorinated hydrocarbons can be recovered by regeneration with steam or with benzene.

Waste streams containing large concentrations of organics cannot be economically treated by carbon adsorption which is limited to the removal of small quantities of organic contaminants.

Combustion

Combustion processes are often feasible in disposing of petrochemical wastes that are too concentrated or too toxic for other treatment methods. Combustion may either be direct or catalytic, depending on the waste being oxidized. Incineration and submerged combustion are both direct combustion methods and both have been used by the petrochemical industry. Submerged combustion occurs in a specially-designed burner (Weisman, 1953). This device has been used successfully for total or partial evaporation of waste streams and for concentrating dissolved solids. The products produce an effluent which has reuse value or is more treatable.

For example, a nylon waste stream was reduced 75 percent, the remainder of which was mixed with other process streams and treated biologically (Remy and Lauria, 1958). Similarly, a polymeric waste stream (containing suspended synthetic rubber particles, organic solvents, inorganic salts, and synthetic detergents) which was not amenable to biological treatment was reportedly treated by submerged combustion (Weyermuller and Davidson, 1958). This waste stream was evaporated to about 10 percent of its original waste volume, with the resulting slurry dried on a drying bed. Also, volatile organic compounds in the polymeric waste, such as alcohols and amines, have been burned so that no odors were detected in the surrounding areas. Submerged combustion also has been used to remove toluene and cyclohexane from an effluent which was later filtered and lagooned (Meinhold and Mandele, 1960).

The wide variety of wastes listed in Table VII-8 demonstrates the extent to which incineration is used by the petrochemical industry. The composition of both liquid and solid wastes dictates the supplementary fuel requirements. Recently, fluidized bed incinerators have been used for burning refinery wastes (Gossom, and Stevens, 1965) and are reported to provide better controlled combustion. Additionally, excess biological solids from waste treatment processes are often incinerated in conjunction with the petrochemical wastes. The advantages of incineration include the ability to treat concentrated and toxic waste streams as well as corresponding reduction of relatively large volumes of waste to small volumes of innocuous ash. However, incineration often simply converts a water pollution problem into an air pollution problem. Suitable equipment must be installed on incinerators to control the discharge of pollutants to the atmosphere. Sulfur compounds such as hydrogen sulfide and sulfur dioxide are common air pollutants which may be released when petrochemical wastes are incinerated. Fly ash also can be released when tars containing inert materials are burned (Garrett, 1959). These air pollutants should be removed from the incinerator effluent gases. When an incinerator is designed, provisions should also be made for the disposal of ash produced by the combustion process. The properly designed incineration system considers time, temperature, and turbulence. Sufficient residence time should be provided to permit complete oxidation of the organic

TABLE VII-8

DESTRUCTION OF PETROCHEMICAL WASTES BY COMBUSTION METHODS

Combustion Process	Waste	Remarks	Ref
Incineration	Liquid wastes from manuf. of ammonia, urea, nylon intermediates, ethylene glycol, methylamines, methacrylates	Wastes concentrated to 50% organic content-no auxiliary fuel required. Steam atomized burners	67
Incineration	Organic tars, catalyst complexes	Metals must be collected when catalysts are burned.	47
Incineration	Liquid Wastes containing hydrocarbons, high-boiling degradation products, tars from nylon intermediate manuf.	-	23
Incineration-1600 °F	Liquid from acrylonitrile manuf. containing acetonitrile and cyanides + slop oils + phenolic resin waste (inorganic)	Nitrile wastes have high fuel value. Provision for auxiliary fuel gas was made.	101
Incineration-1500 °F	Two soot streams from acetylene manuf.; still residues from acrylonitrile and vinyl chloride processing; stripping steam with acrylonitrile	Natural gas used as auxiliary fuel. Flow and organic content of waste fluctuates greatly.	108
Incineration	Heavy sludge, acid, sulfonated tars from benzene plant. General refuse, scrap plastic	Solid wastes fed first, then liquid.	87

TABLE VII-8 (Continued)

DESTRUCTION OF PETROCHEMICAL WASTES BY COMBUSTION METHODS

Combustion Process	Waste	Remarks	Ref
Incineration	Styrene sill residues	Mixed with fuel oil and used in heating furnaces	87
Incineration	Organic acids, salts, anhydrides, Hydrocarbons and chlorinated hydrocarbons from manufacture of chlorinated organics	Natural gas fuel used in a vortex burner. Wastes neutralized with ammonia prior to incineration to prevent corrosion	76
Incineration 800-900 °C	Sludges containing oil, solids from separators, clarifiers, tank bottoms	Fluidized-bed furnace	66
Incineration	Biological sludges	-	-
Incineration	Vent gases - H_2S, mercaptans	-	7
Incineration	Spent caustic - 50% phenols	Fuel oil used as auxiliary fuel	7
Incineration	Spent sulfuric acid sludge	-	7
Incineration	High- and low-boiling organics from nylon manuf.	-	113
Submerged combustion	Organic acids and ketones from nylon manufacture	-	96

TABLE VII-8 (Continued)

DESTRUCTION OF PETROCHEMICAL WASTES BY COMBUSTION METHODS

Combustion Process	Waste	Remarks	Ref
Submerged Combustion	Cyclohexane and toluene from organometallic processing	Conc. effluent is pressure-filtered and lagooned	82
Submerged Combustion	Hydrocarbons and polycyclic aromatics from ethylene and acetylene production	Stripped hydrocarbons are incinerated, stripped effluent goes to biological treatment	66

material, the temperature should be high enough for the reaction to proceed, and the system should be sufficiently turbulent to insure that the oxygen in the air is contacted with the dissolved organic material (Ross, 1967).

Filtration

Filtration processes are used to remove and concentrate solid or oily materials from a waste stream. A filter can be specifically designed to remove small quantities of these materials as a final step in waste treatment or it may be used to concentrate a waste so that further treatability of wastewater will be enhanced. Some typical applications of vacuum and sand filtration processes are listed in Table VII-9.

Filtration is a normal pre-treatment step in the preparation of a petrochemical waste for deep well injection. Such filtration facilities must be provided in order to prevent the clogging of deep wells with suspended solids. Sludges produced by chemical coagulation and clarification of petrochemical wastes are often vacuum filtered to reduce their volume for easier handling and disposal. Precoat vacuum filters have also been used to remove solids from spent sulfuric acid catalysts which are subsequently sold for use in fertilizer manufacture (Federgreen and Weinberger, 1957). If effluent standards imposed on a petrochemical plant are particularly stringent, a polishing filter employing sand filtration can be used to remove additional suspended material (Wilson, 1960). The practicality of filtering a wastewater should be based on laboratory or pilot plant investigations. Such investigations establish the criteria which will dictate the design of the filter.

Miscellaneous Treatment Methods

Certain other physical processes such as evaporation and induced foaming have been used as methods of treating some petrochemical wastewaters. Dilute wastewaters containing small quantities of salt and miscellaneous organic compounds are evaporated in a 64-acre lagoon in Texas (DeRopp, 1951). Solar evaporation is feasible if the petrochemical plant is located in an area with a low annual rainfall and a relatively warm climate. Spraying the wastewater in the air will expose a greater water surface to the atmosphere and will increase the rate of evaporation (Gloyna and Malina, 1962). Evaporation of wastewaters can also be accomplished in specially designed evaporating units. A refinery in Germany has used evaporation to reduce the volume of foul water condensates containing sulfides and phenols by 10 percent (Huber, 1967). The mixture of steam and volatile pollutants from the evaporator is used as atomizing steam in the burners of a distillation unit. This evaporator has effectively removed all of the sulfur compounds from the condensates and requires very little maintenance. A similar type of

TABLE VII-9

TYPICAL FILTRATION APPLICATIONS IN PETROCHEMICAL WASTE TREATMENT

Waste	Vacuum Filter		Sand Filter		Others	Ref
	with precoat	without precoat	with pressure	without pressure		
Acids, aromatics from detergent manuf.; nitriles; pretreatment for injections				X		101
Biological sludges from biological treatment processes		X		X		5
Neutralized effluent from submerged combustion unit treating organometallic wastes			X			82
Oil-Ferric hydrate sludge					X Chamber press	4
Oils from styrene and butadiene production					X	77
Oils in separator effluents	X				X Clay and coke X	5

TABLE VII-9 (Continued)

TYPICAL FILTRATION APPLICATIONS IN PETROCHEMICAL WASTE TREATMENT

Waste	Vacuum Filter		Sand Filter		Others	Ref
	with precoat	without precoat	with pressure	without pressure		
Stable oil-water emulsions from oil separator and impounding basin	X					90
Sludge from coagulation of wash waters and spent caustics from many petrochemical processes	X					90
Secondary effluent from activated sludge				X		116
Wastes from cumene phenol and acetone production--pretreatment for injections			X			101
Zinc-containing sludge from coagulating acrylic fiber wastes	X					101
Spent acid catalyst from Methylstyrene production	X					35

evaporation process has been used to reduce the volume of a nylon waste stream containing organic acids and metal salts prior to incineration (Walker, 1958).

The separation of surface-active agents from wastewater by induced foaming has been investigated in laboratory and pilot plant studies (Brunner and Stephan, 1965). Most of these studies have been concerned with the removal of synthetic detergents from domestic wastes (McGauhey and Klein, 1961). There is little published data available concerning foam separation, and no full-scale treatment plants presently are operating in the United States. It has been demonstrated that the surface-active agents naphthylamine and naphthoic acid, which have little or no foaming ability, could be removed from solution by adding a foaming agent and inducing frothing (Karger and Rogers, 1961). It is possible that there may be special applications in petrochemical waste treatment which might require foaming techniques although laboratory and pilot plant investigations are necessary to establish the applicability.

CHEMICAL TREATMENT METHODS

Many chemical methods are used in the partial treatment of specific petrochemical waste streams. The most common include neutralization, precipitation-coagulation, and oxidation. These processes as well as some less frequently used methods will be discussed herein.

Neutralization and pH Adjustment

Neutralization is often required in treating petrochemical wastes since analysis of petrochemical waste characteristics incidates that many process waste streams are highly acid or alkaline. Neutralization may be desired for several reasons, including

a) preparation of a waste for biological treatment,

b) preparation of a waste for direct discharge,

c) pretreatment for efficient coagulation,

d) prevention of attack and corrosion of conveyance or process equipment, and

e) prevention of unwanted precipitation of waste components.

Neutralization implies the adjustment of a wastewater pH to values at or near neutral pH, i.e., pH 7. It should be noted that adjustment to certain pH values is commonly used to facilitate coagulation and precipitation.

Typical applications of neutralization and pH adjustment requirements for treating petrochemical wastes are tabulated in Table VII-10. In most of the cases cited, neutralization is used as a primary treatment step, with coagulation and settling of the waste often following. Types of wastes generally neutralized include (a) dilute acid or alkaline wash waters from many petrochemical processes; (b) spent caustics from caustic treating operations; (c) acid sludges from alkylation, sulfonation, sulfation, and acid treating processes; and (d) spent acid catalysts (Anon., API, Vol. III, 1958).

Coagulation and sedimentation of wastes is more effective if the pH of the waste is adjusted to the optimum value for the coagulant used. Oil-in-water emulsions can sometimes be broken by pH adjustment alone, and when coagulation is used to break emulsions, prior pH adjustment of the wastewater is usually required.

Spent caustic wastes are often neutralized with acidic waste streams, sulfuric acid being the most commonly used neutralizing agents (McRae, 1959). Acid sludges are normally hydrolyzed to free acids prior to their use as neutralizing agents. The neutralization of a phenolic spent caustic solution separates it into two phases, an aqueous phase containing the sodium salt of the neutralizing acid and an oily phase containing phenolic compound, called "acid oil" (Beychok, 1967). Sulfides in spent caustics are released as hydrogen sulfide during the neutralization process and the "acid oil" requires further treatment to remove the large quantities of phenolic compounds. The salt solution from caustic neutralization may be suitable for discharge without treatment, but since it still contains some phenolic compounds, additional treatment is normally required (Anon., API, Vol. III, 1958). Spent caustic neutralization with an acid can be designed as a batch or a continuous system. A typical installation for the neutralization of spent caustic solutions with acid is schematically illustrated in Figure VII-2. In order to liberate the acid oils and hydrogen sulfide most efficiently, the system is operated at a value of pH five (Anon., API, Vol. III, 1958).

The carbon dioxide in flue gases can also be used to neutralize spent caustic solutions in a manner similar to that described for strong acids with sodium carbonate being the predominant salt in the aqueous phase. Most of the phenols can be removed from a caustic waste if flue gas stripping is continued for a sufficient period (Anon., API, Vol. III, 1958). Flue gas neutralization is feasible provided that the gases are available at high enough pressures so that no blower is required to inject them into the spent caustic solution (Anon., API, Vol. III, 1958). Some catalyst regenerators supply flue gas at high enough pressures to satisfy this requirement. Spent caustic neutralization with flue gas is often operated as a batch process. This type is shown in Figure VII-2. The

TABLE VII-10

TYPICAL APPLICATIONS OF NEUTRALIZATION OR pH ADJUSTMENT TO PETROCHEMICAL WASTES

Process or Products Manufactured	Waste Components	Agent	Remarks	Ref
Acid treating processes	Spent sulfuric acid	Spent caustic		6
Adipic acid	Organic acid	Ammonium hydroxide		22
Alkylation, sulfonation for detergents, etc.	Sulfonic acids Sulfonates	Lime	Coagulation follows	103
Amines, amides				26
Butadiene	Cuprous ammonium acetate	Spent caustic		104
Butadiene, olefins			Follows coagulation	26
Catalytic processes	Aluminum chloride phosphoric acid	Lime		6
Chemicals for lubricating oils			Coagulation follows	26
Freon	Inorganics			113
Herbicides	Chlorinated hydrocarbons	Lime		26

TABLE VII-10 (Continued)

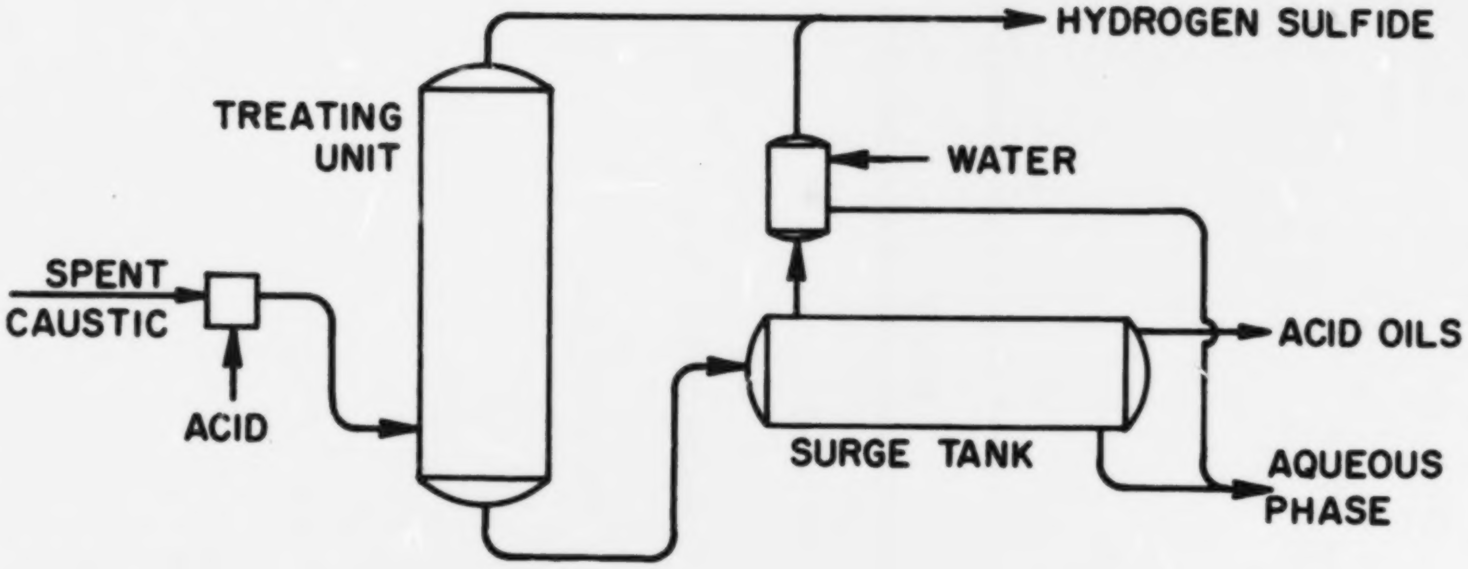
TYPICAL APPLICATIONS OF NEUTRALIZATION OR pH ADJUSTMENT TO PETROCHEMICAL WASTES

Process or Products Manufactured	Waste Components	Agent	Remarks	Ref
Many Petrochemical operations	Emulsified oils	Lime	For coagulation	61 5
Mixed Petrochemicals	Aliphatic acids, esters, alcohols; aromatics; amines	Soda ash	For biological treatment	106
Mixed Petrochemicals--olefins, aromatics, nitriles, resins, detergents, etc.	Oily wastes	Lime	After biological treatment as coagulant aid	102
Orlon	Mixed organics and inorganics			113
Phenol, salycylic acid, rubber chem., aspirin	Mixed organics	Lime	Coagulation follows	146
Polyethylene	Hexane, catalyst alcohols		pH adjustment, clarification follows	104
Polyvinylchloride plastics		Lime	Coagulation follows	26

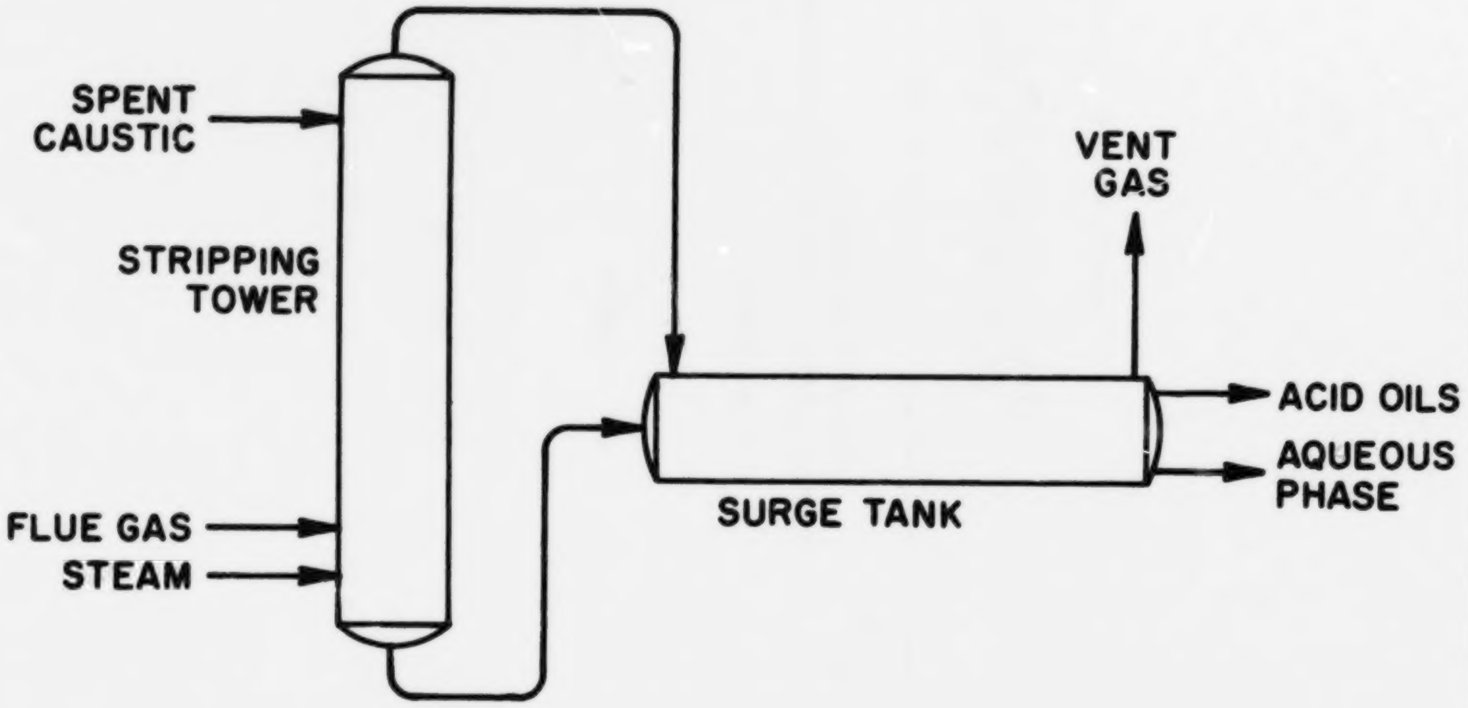
TABLE VII-10 (Continued)

TYPICAL APPLICATIONS OF NEUTRALIZATION OR pH ADJUSTMENT TO PETROCHEMICAL WASTES

Process or Products Manufactured	Waste Components	Agent	Remarks	Ref
Spent caustics from caustic treating operations	Spent caustic			6
Styrene	Acid wastes	Waste alkaline sodium aluminate	Sedimentation follows	77
Tetraethyl lead	Lead; sodium chlorides, sulfates; Ethyl chloride		For coagulation	51


HYDROGEN SULFIDE
TREATING UNIT
WATER
SPENT CAUSTIC
ACID
ACID OILS
SURGE TANK
AQUEOUS PHASE

(a) ACID NEUTRALIZATION


SPENT CAUSTIC
VENT GAS
STRIPPING TOWER
ACID OILS
AQUEOUS PHASE
SURGE TANK
FLUE GAS
STEAM

(b) FLUE GAS NEUTRALIZATION

FIGURE VII-2

SPENT CAUSTIC NEUTRALIZATION

(Reference 81)

spent caustic flows downward countercurrent to the flue gas and the caustic solution is recycled until neutralization is complete (Anon., API, Vol. III, 1958). Normal neutralization periods range from 16 to 24 hours with a corresponding carbon dioxide utilization of 25 to 50 percent. The effluent from flue gas neutralization will require the same type of treatment as those from acid neutralization. The aqueous phase will usually contain carbonates, bicarbonates, sulfates, sulfites, thiosulfates and small quantities of phenolics (Anon., API, Vol. III, 1958).

Neutralization and pH adjustment of other aqueous waste streams are usually carried out in simple neutralization tanks which provide for mixing of the reactants, allowing sufficient time for the neutralization reaction to approach completion. Spent acid catalysts and sludges have been spread in pits filled with lime, limestone, or oyster shells for neutralization (Anon, API, Vol. III, 1958). The most economical method of neutralization depends on the character and quantity of the waste being neutralized and the source and supply of the neutralizing agent.

Coagulation-Precipitation

Coagulation and precipitation are used to remove suspended and colloidal waste materials and their applications for various petrochemical wastes are listed in Table VII-11. It should be noted that coagulation is always followed by some type of solids-separation process. Gravity separation in conventionally designed clarifiers is the most common method, but flotation and filtration are also used to remove agglomerated material. The most commonly used coagulants are hydrated aluminum sulfate (alum), ferrous sulfate, and ferric salts. Coagulant dosages and optimum coagulation pH ranges are usually determined in laboratory investigations. After the coagulants are added to a waste, sufficient time must be provided to allow the buildup of settleable floc particles. The conventional coagulation system utilizes a rapid-mix tank followed first by slow agitation of the mixture in a flocculation tank to promote the growth of floc particles, then by sedimentation. The sludge-blanket clarifier, which provides mixing, flocculation, and settling in the same unit, has had many industrial applications because of its compact dimensions. This type of unit recycles preformed floc which aids in the development of new floc particles and enhances the entrapment of colloids. Occasionally, some form of coagulant aid is required to help form a good-settling floc by promoting bridging between floc particles and rendering the floc more settleable. The most common coagulant aids are activated silica and the organic polyelectrolytes. There are three types of these polyelectrolytes: a cationic, which adsorbs on a negative colloid or floc particle, an anionic which replaces the anionic groups on a colloidal particle and permits hydrogen bonding between the colloid and the polymer, and the non-ionic which adsorbs and flocculates by hydrogen bonding between the solid surfaces and the polar groups in

TABLE VII-11

COAGULATION AND SEDIMENTATION OF PETROCHEMICAL WASTES

Product or Process	Waste Components (If known)	Coagulant(s)	Remarks	Ref
Acrylic Fiber	Zinc	Lime, ferrous sulfate	pH 9.3	101
Alkylation, Sulfonation	Organic sulfonates	Lime, ferrous sulfate		103
Butadiene; Olefins		Lime, alum		26
Copolymer Rubber	Latex			77
Many petrochem processes	Emulsified oils	Alum, ferrous sulfate, ferric chloride - sodium silicate aid	Effluent oil 5-10 ppm effluent turbidity 10-20 ppm	61
Nylon monomers		Ferric chloride	High coagulant concentrations required opt. pH = 4.5	44
Polyvinyl chloride Plastics		Alum	>90% S.S. removed; 60% BOD_5 removed	26

TABLE VII-11 (Continued)

COAGULATION AND SEDIMENTATION OF PETROCHEMICAL WASTES

Product or Process	Waste Components (If known)	Coagulant(s)	Remarks	Ref
Refinery and Natural Gas Liquids		Ferric sulfate nontoxic polyelectrolyte	80% oil rem. 75% S.S. rem. 44% COD rem. 34% Sulfides rem.	117
Refining Process	Oils	Alum, activated silica	flotation, 94% oil rem.	98
Refining Process	Oil emulsions, sulfuric acids, napthenic acids, phenols, fatty acids, sodium salts	Lime (alum, iron sulfate added if needed)	95% turbidity removed; 60-85% S.S. removed Effluent oil <5 ppm	89
Refining Process	(Same as above)	Aluminum and ferric salts	90-95% oil rem. 35% COD rem.	66
Synthetic Rubber		Alum	82.5% S.S. rem. 82.5% BOD_5 rem.	28
Tetraethyl Lead	Lead, ethyl chloride, sodium chlorides, sulfates, sulfides	Ferrous sulfate		51

the polymer. The most effective coagulant aid can be determined only through a series of laboratory tests.

A common application of coagulation in the petrochemical industry is the removal of emulsified oils from waste streams. Almost every type of coagulant has been used to treat emulsions, as illustrated in Table VII-11. Effluent oil concentrations from coagulation processes have been reported as low as five mg/l with oil removal by coagulation usually in the range 75-85 percent (Beychok, 1967). Suspended solids and turbidity removals are often as high as 90 percent, depending upon the characteristics of the wastes being treated. If large quantities of suspended and colloidal organic materials are present in a wastewater, coagulation and sedimentation can result in substantial COD and BOD removals. However, most petrochemical wastes contain primarily dissolved organic compounds which are not removed to any extent by coagulation.

Coagulation is also effective in enhancing flotation of emulsified oils and suspended material. The addition of alum and activated silica to a refinery waste being treated by flotation increased the oil removal from 62 percent to 94 percent (Rolich, 1954). The large floc particles formed by the coagulation process provide more surface area for air bubble attachment, thus increasing the flotation cell efficiency.

Coagulation has also been used to remove metals such as lead and zinc from petrochemical wastes. Water-soluble alkyl-aryl sulfonates can be removed from wastewater by coagulation with lime, which forms insoluble precipitates. Settling of the precipitate can be enhanced by adding ferrous sulfate (Schindler, 1949; 1951). Low concentrations of sulfide can be precipitated with zinc chloride, ferric chloride, or copper sulfate. This precipitate can then be removed by flocculation of the precipitate (Anon., API, Vol. III, 1958).

Provisions must be made for the disposal of the sludges formed by these settled precipitates. Landfills are the most common form of inorganic sludge disposal. Some organic sludges are dewatered and subsequently incinerated or buried. Anaerobic digestion is rarely used by the petrochemical industry for organic solids treatment.

Oxidation Processes

A variety of oxidation processes have been used in the treatment of petrochemical wastes. Combustion processes were discussed with the physical treatment methods, but catalytic oxidation, considered to be a combustion process, is discussed here. Oxidation processes are used to treat both organic and inorganic contaminants using oxygen or other chemicals as the oxidizing agents. Oxidation processes as applied to various petrochemical wastes are tabulated in Table VII-12. The following discussion briefly describes the most commonly used oxidation methods.

TABLE VII-12

OXIDATION PROCESSES USED IN PETROCHEMICAL WASTE TREATMENT

Product or Process	Waste Components (If known)	Type of Oxid. Process	Remarks	Ref
Acrylic fibers, nitriles	Cyanides	Ozone	Opt. pH 11-12	110
Acrylic fibers	Dimethylamine Dimethylformamide	Catalytic oxidation	Pt. catalyst, 310°C, combined with direct combustion	109
Acrylic fibers, nitriles	Cyanides	Chlorination	1-2 hr treatment time pH 8.5 required	6
Caustic treating operations	Sulfidic Spent Caustics	Air and steam	Oxidizes sulfides to thiosulfates and sulfates	80 13
Ethylene glycol	-	Catalytic oxidation	Copper-chromite catalysts 97% organic destruction	59 33
Mixed petrochemicals	Hydrocarbons	Catalytic oxidation	Metal oxide catalysts	107
Mixed petrochemicals	0.5-1.0% Organic from column heads	Catalytic oxidation	575°C Pt. catalyst added to control oxidation	62
Mixed petrochemicals	3-5% Organic acids	Thermal cracking	800°C, natural gas	67

TABLE VII-12 (Continued)

OXIDATION PROCESSES USED IN PETROCHEMICAL WASTE TREATMENT

Products or Process	Waste Components (If known)	Type of Oxid. Process	Remarks	Ref
Synthetic Rubber	Probably unsaturated H.C. (some chlorinated)	Ozonation	Opt. pH 12.6, 90.5% COD reduction	
Nylon intermediates	16% NaCl, 0.5% metal salts, 1% misc. organics	Air	Converts metals to insoluble hydroxides	23
Phenol, resins, refining crude	Phenolics	Ferrous salts and hydrogen peroxide	Expensive	32
Phenol	Sulfite liquors	Chlorine		32
Phenol	Sulfite liquors	Ozone	Opt. pH 12	88
Phenol -	Sulfite liquors	Air-iron catalyst in liq.	Aerations in venturi units 99.9% SO_3 removed-11 hr	116
p-Cresol	Sulfite liquors	Air	Mixco agitator w/ sparge ring	26
β-Naphthol	Sulfite liquors	Air	Mixco agitator w/ sparge ring	-
Refinery	Petroleum products	Ozonation	75-85% removal of petrol. prod. 16 hr detention	91

The oxidation of sulfides to sulfates using steam and air is an effective method of treating wastes containing such compounds. Sulfides cannot be effectively steam-stripped from spent caustics since sodium sulfide does not hydrolyze appreciably under those conditions. While wastes containing ammonium sulfides can be steam-stripped, the hydrogen sulfide stripped from such wastes can often cause air pollution problems. Oxidation of sulfides to thiosulfates and sulfates can be an economical method for the disposal of these compounds; however, wastes containing high concentrations of phenol cannot be treated by these methods because phenols interfere with sulfide oxidation.

The chemistry and theory behind the oxidation of sulfides is well documented (Beychok, 1967). Most sulfide oxidation units presently used are patented designs. The design criteria and operation conditions for several types of these units are listed in Table VII-13. All of the units mentioned oxidize 100 percent of the influent sulfides, but if large quantities of mercaptans or mercaptides are present in the waste, a reoxidizer may be required to insure complete oxidation (Beychok, 1967). The reoxidizer should be operated at a temperature of 130-150°F with a pressure of 50 psi to prevent mercaptan stripping. The data in Table VII-13 indicates that sulfides can be oxidized to thiosulfates more easily than to sulfates. It is possible that some sulfate was produced in the towers, but to obtain maximum converstion, low sulfide loadings are required. The oxidation of sulfides is a liquid phase process with a typical unit shown in Figure VII-3. Temperatures at the top of the oxidation tower are normally kept below 200°F for ammonium sulfide feeds to prevent stripping of hydrogen sulfide, since oxidation is not as effective in the vapor phase (Beychok, 1967). Heavy oils should be eliminated from the waste prior to oxidation since pilot plant studies indicated that five percent of such oil could decrease the oxidation rate by 50 percent.

Catalytic oxidation has been used to treat petrochemical wastes containing various toxic organic compounds not amenable to biological degradation. It is usually applied when the fuel value of a waste is too low for conventional incineration. The process was originally designed to operate in the vapor phase, but it has been successfully applied to aqueous wastes. Laboratory investigations have shown that dilute aqueous organic wastes could be effectively oxidized at temperatures below 600°C by using a copper-chromate catalyst (Green and Moses, 1952). These studies indicated that sulfur compounds could seriously contaminate the catalyst. Investigations have demonstrated that hydrocarbons could be oxidized also by using metal oxide catalysts (Stein, et. al., 1960). The following examples indicate the application of this treatment technique to petrochemical wastes.

TABLE VII-13

DESIGN AND EFFICIENCY OF SOME SULFIDE OXIDATION UNITS

(Reference 12)

Oxid. Products	Tower Temp. (Top) (°F)	Feed $(\frac{\text{lb Sulfide}}{\text{min}})$	Air Flow $(\frac{\text{lb air}}{\text{lb S oxidized}})$	Detention Time (hr)	Pressure (Top) (psia)	Sulfur Oxidized $(\frac{\text{lb/hr}}{\text{ft}^3\text{ tower}})$	Remarks
100% Thiosulfite	185-250	1.4-11.7	7.3-12.2	1.1-7.9	50-79	0.29-0.39	Concurrent air-water flow, no catalyst
54% Thiosulfite 46% Sulfate	230	0.68	6.8	3.87	75	0.03	"
44% Thiosulfite 56% Sulfate	239	0.17	27.0	3.31	57	0.01	"
37% Thiosulfite 63% Sulfate	239	0.08	57.5	6.62	57	0.05	"
100% Sulfate	265	0.73	28.4	3.52	72	0.035	Countercurrent air-water flow, Copper chloride catalyst 10 mg/1 as Cu*

---

* The Sulfide Feed of 11.7 lb/min corresponded to the tower with the 7.9 hr Detention Time. If this tower were omitted, the range of Sulfide Feed would be 1.4-5.5 lb/min and the Detention Time would be 1.1-1.4 hr. All other design parameters for this tower were in close agreement with the others oxidizing sulfides to thiosulfates

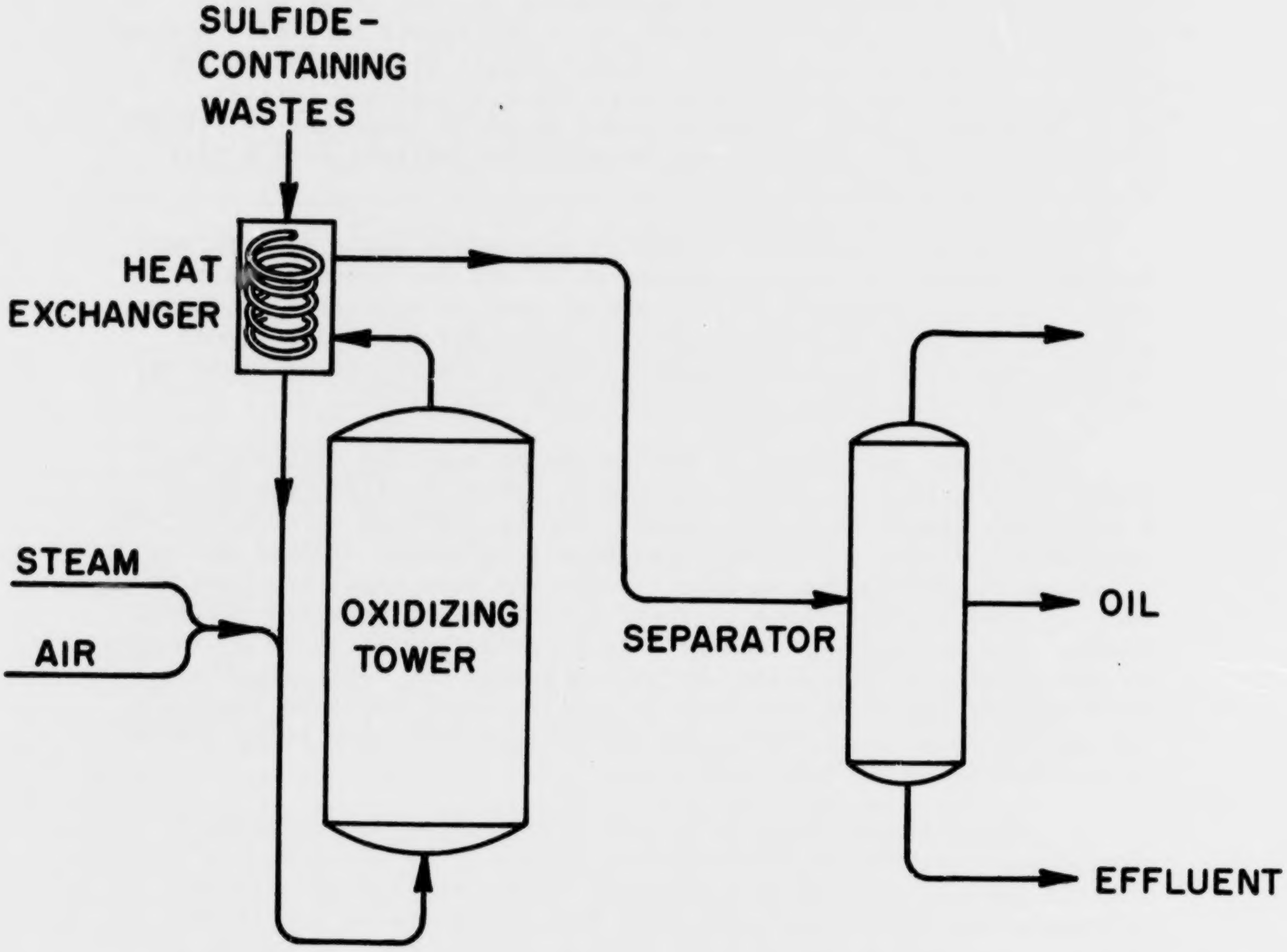

SULFIDE-
CONTAINING
WASTES
HEAT
EXCHANGER
STEAM
AIR
OXIDIZING
TOWER
SEPARATOR
OIL
EFFLUENT

FIGURE VII-3
SULFIDE OXIDATION UNIT
(Reference 13)

Solvent recovery heads for acrylic fiber manufacture have been successfully oxidized by using a combination of catalytic and direct combustion techniques (Taylor and Bodurtha, et. al., 1961). The influent waste contained 3,000 mg/l dimethylamine and 1,000 mg/l dimethylformamide. Oxidation at 310°C using a platinum catalyst reduced the concentration of dimethylamine to five to 10 mg/l in the effluent and reduced the waste BOD_5 by 1,000 pounds per day. Another catalytic oxidation unit treats organic wastes in a concentration range of 0.5 to 1.0 percent organics, using a platinum catalyst at 575°C (Hyde, 1965). Steam is added as it is necessary to prevent runaway reactions. The platinum catalyst is replaced once a year at this installation.

Catalytic oxidation offers an economical means of treatment for small volumes of organic wastes which are not susceptible to other treatment processes. The initial cost of catalytic oxidation units may be 20 to 30 percent greater than that for conventional incinerators, but for dilute organic wastes the operating costs may be 15 to 20 percent less (Anon., API, Vol. III, 1958).

Certain petrochemical wastes can be oxidized directly by aeration techniques. Wastes containing sodium sulfite, which has a very high immediate oxygen demand, can be oxidized by bubbling air through the system. Various types of air diffusion devices can be utilized to oxidize the sulfite liquors and iron catalysts have been used in some installations to speed the oxidation reaction (Wilson, 1960). The oxidation of the sulfite to sulfate will cause an increase in the acidity of the waste, requiring subsequent neutralization. Diffused air has also been used to oxidize metal salts to insoluble hydroxides in a nylon waste, the metal hydroxides then being removed by sedimentation (DeRopp, 1951).

Chlorine and ozone have both been applied in oxidizing phenol and cyanides in petrochemical wastes. The oxidation of phenols must be carried to completion to prevent the release of chlorophenols which are responsible for objectionable tastes and odors in drinking water at very low concentrations. An excess of chlorine is usually required because of the reaction with various other chemical compounds such as ammonia, sulfides, and various organics which can interfere with the chlorination process. An excess of chlorine to phenol ratio up to 50:1 is often required for complete phenol oxidation (Anon., API, Vol. III, 1958). To prevent the formation of chlorophenols, the pH of the waste is kept at seven or higher and the usual reaction time required is one to two hours. Chlorine can be used either as free chlorine or as hypochlorite.

Cyanides can be oxidized to carbon dioxide and nitrogen by chlorination. The wastewater must be kept at a pH value greater than 8.5 during treatment to prevent the release of toxic cyanogen chloride (Anon., API, Vol. III, 1958). The reaction time usually is one to two hours and the process is subject to the same interferences as in phenol chlorination. Batch treatment with hypochlorite is used for small volumes of waste while continuous systems normally use chlorine gas.

Chlorine dioxide which has been investigated as an oxidant for phenols and cyanides (Anon., API, Vol. III, 1958), seems to have several advantages over chlorine or hypochlorite which include (a) no chlorophenols produced by undertreatment of phenols, (b) less rigorous process control required, (c) no requirement for pH adjustment, (d) shorter reaction times are needed, and (e) less trouble with formation of cyanogen chloride during cyanide oxidation. The chief disadvantage of chlorine dioxide is its high cost (Anon., API, Vol. III, 1958).

Ozone has also been proposed as an oxidizing agent for phenols, cyanides, and unsaturated organics, since it is a considerably stronger oxidizing agent than chlorine. The chief disadvantage is the high initial cost of the equipment required for ozone generation (Anon., API, Vol. III, 1958). Ozone has several advantages, the most important being its ability to rapidly react with phenol and cyanide. The optimum pH for phenol destruction is pH 11.4 and ozone is added as a one to two percent gaseous solution (Anon., API, Vol. III, 1958). Thiocyanates and cyanides can also be effectively oxidized in a waste containing phenols (Niegowski, 1953). Cyanides are also ozonated at an influent pH of 11 to 12 which drops to approximately pH eight. (Tyler, *et. al*., 1951). Thiocyanates, sulfates, sulfides, and unsaturated organic compounds will also exert an ozone demand which must be satisfied. This demand serves as the basis of design for an ozonation unit treating a wastewater containing these compounds (Anon., API, Vol. III, 1958). Sulfides also can be removed from a wastewater which is to be ozonated by air stripping them at low pH values, thus economically reducing the ozone demand (Niegowski, 1953). The pH of the wastewater can then be raised to the appropriate level required for optimum ozonation. Recent investigations at The University of Texas at Austin have indicated the applicability of ozonating wastes from the manufacture of chlorinated hydrocarbons. The data obtained from laboratory ozonation studies are shown in Table VII-14. The optimum pH for ozonation of this wastewater was found to be 12.6, and as much as 90 percent of the waste COD was removed. This waste contains large quantities of unsaturated hydrocarbons, which are readily amenable to ozonation. Ozonation of a wastewater can be either a batch or continuous operation, depending on the characteristics of the waste and the waste flow rate.

TABLE VII-14

OZONATION OF CHLORINATED HYDROCARBONS

(Reference 38)

Ozone Dosage (mg/1)	pH Initial	COD Raw Waste (mg/1)	COD Treated Waste (mg/1)	COD Reduction (%)
994	12.2	3,340	1,410	57.8
2,530	12.6	"	900	73
2,700	7.0	"	1,460	56.5
3,920	12.6	"	745	77.5
4,640	12.6	"	450	86.5
5,400	12.6	"	314	90.5

Oxidation of phenols using hydrogen peroxide and ferrous salts has been investigated in the laboratory (Eisenhauer, 1964). Treatment of the industrial wastes studied produced colored effluents which required additional treatment with alum for color removal. This method is probably not economical for most phenolic petrochemical wastes but may be useful in removing phenols from intermittently discharged low-volume wastes.

Miscellaneous Methods

Ion exchange has been used to remove certain petrochemical pollutants. Quatenary ammonium anion resins were successfully used to remove phenols in laboratory investigations (Anderson and Hansen, 1955). However, regeneration of the resin was difficult, making this method of phenol removal uneconomical for most industrial applications, Ion-exchange, however, has been used successfully to recover salicylic acid from aspirin manufacture effluents (Wilson, 1960). Salicylic acid recoveries of 80 percent were obtained using a caustic-soda regenerated resin and the recovered acid was then reused in the manufacture of aspirin. The only problem associated with this process was a partial physical breakdown of the resin.

Chemical reduction can also be used to treat certain chemical compounds found in petrochemical wastes. The manufacture of phenetole produces an effluent containing p-nitrophenol, an aromatic compound which is toxic, relatively non-biodegradable, and imparts a yellow color to water (Wilson, 1960). The p-nitrophenol is reduced at the source of the process effluent by using iron turnings and sulfuric acid. The reduced organic compounds are biodegradable and colorless.

BIOLOGICAL TREATMENT PROCESSES

Biological treatment of liquid petrochemical wastewaters is usually the most economical method of reducing organic content, toxicity, and objectionable appearance. The treatment of petrochemical wastes using biological methods is considerably more complex than the treatment of domestic wastes and many of the industrial wastes. For example, extensive pretreatment is often required before a petrochemical waste stream can be treated biologically. The following discussion will elaborate on those aspects of petrochemical wastewater characteristics which require special consideration for successful biological treatment. Where available, design and operating parameters from existing petrochemical treatment facilities will be cited.

General Considerations

Biodegradability - The applicability of biologically treating a particular waste is a function of the biodegradability of the dissolved organics present in the wastewater. Almost every organic compound can be degraded biologically under defined environmental conditions provided that sufficient time is available. When considering the economics of a biological treatment system, however, the required degradation time for the organic compounds in the waste is of primary importance. The rate at which an organic compound can be degraded is a function of its availability to microorganisms as an energy supply and as a source for cellular carbon. The molecular structure of an organic compound, the genera and species of microorganism utilizing it as a food source, and the time required for the microorganism to develop the enzymes necessary for successful substrate utilization determine the degradation rate of the compound. Certain molecular structures, especially those not occurring in nature, are difficult to degrade biologically. The amenability of a particular compound to biological degradation is highly dependent on such environmental and growth factors as the nutrient requirements necessary for biological growth, and proper pH and temperature conditions for the microorganisms. The organic compounds must also be in a form suitable for easy biological attack. One of the factors involved in the relative non-biodegradability of oils is their insolubility in water. Oil globules in a wastewater, for example, are not readily accessible to the microorganisms. Proper acclimation is very important since organic compounds which are completely biodegraded by acclimated organisms may be completely resistant to unacclimated microorganisms (Mills and Stack, 1953). To have meaning, a classification system must indicate the biodegradability of a compound by a properly-acclimated microbial system.

The biodegradability classification used in Table VII-15 is strictly an arbitrary system based on the relative biodegradability of selected organic compounds by an acclimated microbial population. These data were obtained from both laboratory and field-scale investigations. The biodegradable class of compounds in Table VII-15 includes substances which are rapidly degraded with little or no biological acclimation required as well as those compounds which require extensive periods for adaptation of the microbial system to the organic substrate. The important consideration is that all of these organic constituents have been shown to be significantly degraded by biological treatment systems or subject to conditions similar to those found in such systems.

The time factor is most significant when considering an adaptive biological system. An organic compound which can be stabilized biologically but which requires time intervals for degradation considerably longer than those available in normal biological treatment systems may be non-biodegradable for all practical purposes. Some of those compounds indicated in Table VII-15 as being resistant to biological degradation may be categorized as such. It is also possible that some of these resistant chemicals might be more readily degraded by specific species of microorganisms.

TABLE VII-15

RELATIVE BIODEGRADABILITY OF CERTAIN ORGANIC COMPOUNDS

(References 74, 75, 89)

Biodegradable Organic Compounds	Compounds Generally Resistant to Biological Degradation
Acrylic Acid	Ethers
Aliphatic Acids	Ethylene Chlorohydrin
Aliphatic Alcohols (normal, iso, secondary)	Isoprene
Aliphatic Aldehydes	Methyl Vinyl Ketone
Aliphatic Esters	Morpholine
Alkyl Benzene Sulfonates w/exception of propylene-based Benzaldehyde	Oil
Aromatic Amines	Polymeric Compounds
Dichlorophenols	Polypropylene Benzene Sulfonates
Ethanolamines	Selected Hydrocarbons Aliphatics Aromatics Alkyl-Aryl Groups
Glycols	Tertiary Aliphatic Alcohols
Ketones	Tertiary Benzene Sulfonates
Methacrylic Acid	Trichlorophenols
Methyl Methacrylate	
Monochlorophenols	
Nitriles	
Phenols	
Primary Aliphatic Amines	
Styrene	
Vinyl Acetate	

---

* Some compounds can be degraded biologically only after extended periods of seed acclimation.

While there is contradictory data relating the molecular structure of a compound to its biodegradability, the amenability of resistance of certain classifications of organic compounds to biological degradation is well documented.

a) Aliphatic or cyclic aliphatics are usually more susceptible to biological degradation than are aromatics.

b) Unsaturated aliphatics, such as acrylic, vinyl, and carbonyl compounds are generally biodegradable (Pahren and Bloodgood, 1961). Styrene, when in solution, is readily degradable, but the degree of breakdown may be adversely affected by its relative insolubility (Harkness and Jenkins, 1958). Organic compounds which contain elements other than carbon in the primary molecular chain, such as ethers, are often resistant to biological attack. Morpholine and tertiary amines are included in this grouping.

c) Molecular size is an important factor concerning the biodegradability of an organic compound. Part of the resistance demonstrated by polymeric and complex molecular substances is attributed to the inability of necessary microbial enzymes to approach and attack susceptible bonds within the compound structure. Insoluble or partially soluble compounds in wastewater are also resistant because of the limited contact surface which is subject to microbial contact.

d) The many possibilities for structural isomerism in substituted organic compounds affect the relative biodegradability of many compound classes. For example, primary and secondary alcohols are extremely biodegradable, while tertiary alcohols are resistant. Alkyl benzene sulfonates using propylene as a base contain a tertiary carbon atom and are consequently resistant while alkyl-aryl sulfonates without tertiary carbon atoms can be completely biodegraded (Ryckman and Sawyer, 1957). The stable bonds of the tertiary carbon atom therefore appear to be just as resistant to biochemical reaction as they are to chemical reaction.

e) The addition or removal of a functional group affects the relative biodegradability of an organic compound. Electrophilic substitution of certain functional groups to aromatics significantly affects the biological amenability of a compound. A hydroxyl or amino substitution to a benzene ring renders the compound more biodegradable than the parent benzene, while a halogen substitution causes it to be less biodegradable.

f) Many organic compounds are completely biodegradable at low concentrations, and bio-static or bio-toxic at higher concentrations, of which phenol is a good example. Slug concentrations of 50 mg/l phenol have been known to exert a toxic effect on biological waste treatment systems (McKinney, 1967); but by providing a completely mixed system and dampening inflow fluctuations, higher concentrations have been successfully treated biologically (Reid and Libby, 1957). A similar response of biological treatment systems to nitriles has been observed.

It should be noted that the biodegradability of individual organic compounds in petrochemical wastewaters may be altered when mixed with other constituents. Organic compounds which tend to polymerize upon contact, such as many of the unsaturated compounds, will probably have an adverse affect on the wastewater biodegradability. Two or more compounds occasionally form a complex which would have a similar effect. It may therefore be necessary to conduct extensive laboratory studies to determine which compounds possibly affect a biological system in this manner, giving a basis for possible stream segregation within the waste collection system.

Finally, the proper acclimation of the microorganisms to a particular wastewater containing one or many compounds should be emphasized relative to accurate biodegradability determination. The lack of "true acclimation" of a biological seed to the wastewater has probably been the main source of contradictory data, misinterpretation and misunderstanding.

Nutrients - Effective biological treatment of any organic wastes requires the availability of essential nutrients for the microorganisms. The predominant organisms in biological treatment systems are bacteria which normally require only trace amounts of nutrients for growth. The mineral nutrients required by bacteria are available in sufficient amounts in most wastewaters. However, nitrogen and phosphorus requirements are considerably more critical, and many petrochemical wastes are deficient in one or both of these elements. If this is the case, these compounds must be added to the wastewater prior to biological treatment.

Nitrogen and phosphorus requirements for biological treatment have been related to the magnitude of the degradable organic content of wastewaters, as represented by BOD. Insufficient nitrogen and phosphorus restrict the rate of organic removal and also may favor the growth of filamentous organisms which cannot be separated by gravity from the wastewater after biological treatment. Generally a BOD:N:P ratio of 100:5:1 will be sufficient to satisfy nutrient requirements for an industrial wastewater. These nutrients must also be in a form which is readily available to the microorganisms. Nitrogen is most readily available in its reduced form, as ammonia, ammonium ion, or amino nitrogen. The reduced form of nitrogen is the form used in building cell protein and oxidized forms of nitrogen and must be reduced by bacterial action prior to assimilation into the cell structure. Organic nitrogen, nitrates, nitrites, and organic compounds containing these nitrogen forms can also be used as a nutrient source by most microorganisms, but a considerable expenditure of energy is required to reduce these forms to ammonia nitrogen. Phosphorus is most readily available to the microorganisms as a phosphate, which is the predominant form of phosphorus in most wastewaters.

Refinery wastes usually contain large quantities of ammonia nitrogen, and may contain sufficient nitrogen to meet the nutrient requirements when mixed with petrochemical wastewaters. Sanitary sewage can often be used as a source of nitrogen and phosphorus for petrochemical wastes. Phosphorus requirements of a petrochemical waste can generally be satisfied by including cooling or boiler blow-down waters within the waste stream.

It is necessary to establish the nutrient requirements for each wastewater considered by measuring the total BOD, analyzing the wastewater for available nitrogen and phosphorus, and providing additional nutrients are required, either by chemical addition or by adding nutrient-rich streams to the system.

Neutralization Requirements - Neutralization or pH adjustment is commonly required in petrochemical wastewater treatment systems. This step is often necessary to provide optimum chemical or biological treatment.

Existing acid or alkaline streams should first be considered as possible pH adjustment sources. Flue gases, normally containing 14 percent carbon dioxide, can often be used to neutralize alkaline wastes. If waste streams are not available, any strong acid can be used to effectively neutralize basic wastes; but cost limitations usually limit the choice to sulfuric or hydrochloric acid. Acid wastes are commonly neutralized in mixing tanks using strongly basic compounds, although downflow or upflow limestone beds are often used. Dual purpose chemicals can often be used as a neutralizing agent and as a nutrient source, such as ammonium hydroxide added to a nitrogen deficient acid waste or phosphoric acid added to a phosphorus deficient alkaline waste. Such practice, when practical, can result in a substantial savings in operating costs. Since neutralization reactions are rapid and sensitive, the neutralization system design must include the following factors:

a) provisions for adequate mixing and holding to allow the reaction to approach completion,

b) provisions for separating and removing any sludge produced, and

c) provisions for adequate neutralization during fluctuating flow-under automatic control.

Some problems have been encountered with automatic pH control systems, particularly when small additions of reagents caused marked changes in pH around a value of 7.0.

Most biological treatment systems cannot operate efficiently at pH values greater than nine or less than five, while optimum process efficiency is usually obtained in the six to eight pH range (Eckenfelder, 1966). Biological systems employing completely mixed aeration basins have a certain degree of buffering capacity. Carbon dioxide produced during biological oxidation, for example, can neutralize as much as 0.7 pounds of caustic alkalinity per pound of COD removed (Eckenfelder, 1966). Consideration of these factors can often reduce pre-neutralization requirements. The buffering capacity of a biological treatment system, its effect on a particular petrochemical waste, and the precise neutralization requirements can only be determined through laboratory or pilot plant studies.

Equalization - Biological and even chemical and physical treatment processes operate most effectively if the composition and volume of the wastewater remains relatively constant. For example, rapid fluctuations in the organic content or flow rate of a waste stream can cause biological treatment plant upsets due to the shock effects on the microorganisms in the system. Equalization is used to dampen these fluctuations in flow and waste composition and minimize the transient effects which adversely affect the process. The holding basin is designed to contain and provide mixing for a selected volume of the wastewater which is pumped from the equalization basin at a constant rate to the treatment facility. The required size of the equalization tank depends on the waste characteristics, the plant operating schedule, and consequent cyclic fluctuations. For example, the maximum to minimum BOD ratio of a wastewater bed to an aerobic biological treatment process should not exceed 3:1 on a 24-hour basis and equalization basins should be designed to limit the BOD fluctuations to this range.

Petrochemical wastes are particularly subject to wide variations in flow and composition and an equalization step is often required. Many smaller and specialized petrochemical processes are batch operations from which sudden releases of wastes can be expected. Often, equalization can also permit the neutralization of wastewaters by premixing acidic and alkaline waste streams which would normally enter the plant waste streams at different times. Various types of construction have been used for equalization basins, including steel tanks and concrete tanks, earth-lined lagoons, and vinyl or butyl-rubber lined lagoons. The type of tank required will depend on the wastewater characteristics and its affect on the construction material. Mixing equipment or baffling is also required to insure adequate tank equalization.

Pre- and/or Primary Treatment - Pre- and primary treatment may be required to remove certain materials from petrochemical wastewaters to prevent adverse effects on a biological treatment system. Maximum limits for selected wastewater characteristics are given in Table VII-16 and biological treatment processes will usually operate at decreased efficiencies if these limits are exceeded.

Oils in wastewater are difficult for the microorganisms to metabolize due to their low solubility (McKinney, 1967). Non-biodegradable oily materials tend to accumulate in biological treatment processes and cause sludge settling difficulties due to their low specific gravity. Suspended solids in wastewater will be incorporated into the biological solids in a waste treatment system (McKinney, 1967). Inorganic and non-biodegradable organic suspended solids will tend to build up in the treatment system, decreasing the proportion of active biological solids and adversely affecting the treatment efficiency. Sulfides react with dissolved oxygen and thus reduce the oxygen available for microbial oxidation of the organics in a biological treatment process, the permissible sulfide concentration normally being a function of the amount of oxygen available. Sulfides at high concentrations can also exert toxic effects in addition to depleting available oxygen, this toxic threshold normally considered to be approximately 250 mg/l as sulfide.

In addition to the characteristics discussed, certain other waste materials may have to be removed prior to biological treatment. Some heavy metals, for example, are toxic to microorganisms at certain concentrations and must be removed or reduced if these thresholds are exceeded. Waste streams containing potentially toxic organic compounds should be separated and treated before discharge into a biological treatment system. A careful laboratory characterization should reveal the type and extent of pretreatment required before a particular petrochemical wastewater can be treated biologically.

Temperature - Temperature effects on biological treatment systems are extremely important and sometimes critical relative to the ability of the system to function properly. High temperature loadings to an activated sludge plant cause a decrease in oxygen solubility as well as an increased oxygen utilization. Summer tempatures therefore represent the most critical stage as far as oxygen supply is concerned, and aeration systems should be designed on this basis. Winter temperatures usually control detention time requirements, however, because of the slower biochemical removal rates of dissolved organic materials. This temperature effect on relative COD removals for a petrochemical waste is shown in Figure VII-4 (Ford, Gloyna and Eckenfelder, 1968).

TABLE VII-16

WASTEWATER CHARACTERISTICS REQUIRED FOR OPTIMUM BIOLOGICAL TREATMENT (MAXIMUMS)

(Reference 25)

Characteristic	Value
Oils, Grease	<75 mg/1
Suspended Solids	<125 mg/1
pH	5-9
Sulfides*	<200 mg/1
Temperature	$<36^{\circ}C$
Heavy Metals	Below Toxic Levels

* Depends Upon Oxygen Available

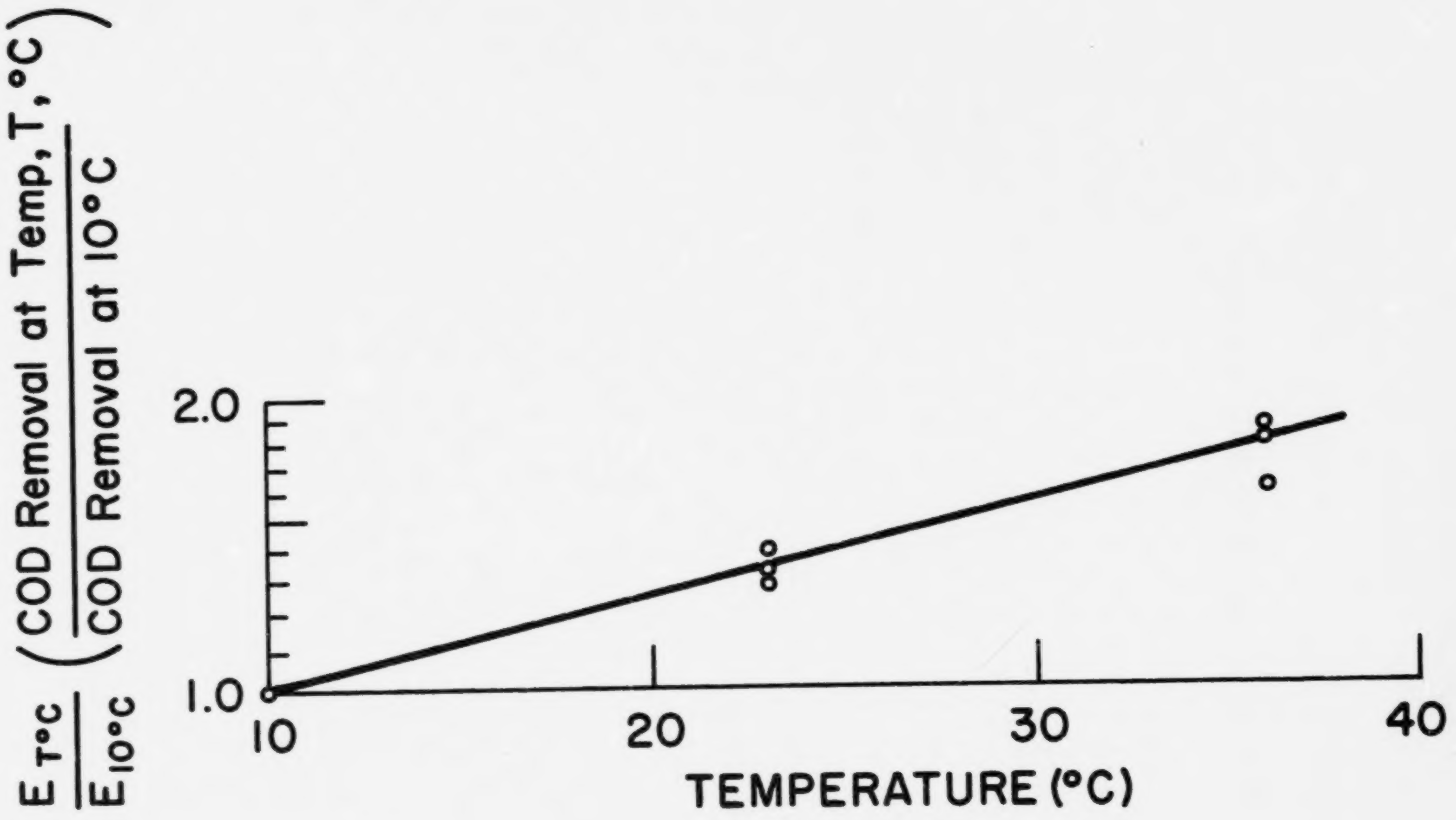


FIGURE VII-4

TEMPERATURE EFFECT ON COD REMOVAL

(Reference 45)

The optimum temperature is approximately 30°C for most aerobic biological treatment systems (Eckenfelder, 1966), while a decrease in plant efficiency has been observed when temperatures exceed 38°C. Some attempts have been made to develop and perfect aerobic systems operating in the 40°C to 65°C range using thermophilic bacteria, but with only moderate success (Ford, 1964). The system operation at these temperatures is extremely sensitive, solids-liquid separation is difficult, and a cloudy effluent is normally produced.

High-temperature petrochemical wastes may require precooling before they are discharged to a biological facility, but cool dilution streams and temperature dissipation in equalization or aeration basins normally preclude this.

Activated Sludge Processes

The activated sludge process is a continuous system where biological growths are mixed with wastewater, aerated, and followed by a biological sludge separation step. A portion of the concentrated sludge is then recycled and mixed with additional waste. This process has been applied very effectively in the treatment of refinery and petrochemical wastewaters.

Although the conventional plug flow system has been used successfully in the treatment of domestic wastes, it has several disadvantages in this design when petrochemical wastes are to be treated. These include

a) erratic effluent quality because of the uneven distribution of effluent solids in the aeration tank and wastewater short-circuiting;

b) localization of certain contaminants, such as phenol, which may exert a toxic effect on the biological solids; and

c) the inability of the plug-flow aeration basin to dampen load variations caused by in-plant dumps or spills, making operation and control difficult.

Completely mixed aeration designs are therefore generally considered for industrial wastewater treatment. In a completely mixed system the aeration tank serves as an equalization basin to dampen load variations and evenly distribute the wastewater and biologically active solids throughout the basin. Since all portions of the tank are mixed, the oxygen utilization rate will be the same throughout the basin, and aeration equipment can be equally spaced. The effluents discuarged from completely mixed activated sludge systems are generally better than those obtained from other biological processes in terms of organic and solids concentrations, although construction and operational costs are usually higher.

Many of the organic compounds present in petrochemical wastes are volatile and consequently stripped from solution in the aeration basin. Laboratory investigations have studied air stripping of volatile organics during the activated sludge process (Englebrecht and Ewing, 1962). These studies indicated that approximately 30 percent of the highly volatile compounds were stripped from solution during the six-hour aeration period normally employed in the activated sludge process. Similar studies indicated that significant concentrations of benzene and nitrobenzene present in a petrochemical waste were air stripped from solution (Eckenfelder and Ford, 1968). The exact removal of volatile organics by this mechanism will be dependent on the type of aeration system as well as the power level in the aeration basins.

The basis for the design of an activated sludge system is predicated on producing and maintaining an environment for microorganisms so that their growth and activity are as near optimal as possible. These parameters include fundamental factors such as temperature, hydrogen ion concentration, and nutrient availability, as well as the following considerations:

a) the organic loading in terms of BOD applied per day per unit wt. of biological solids,

b) the BOD removal kinetics of the specific petrochemical wastewater,

c) the oxygen requirements of the system,

d) the quantity of biological sludge produced including the accumulation of primary sludge, and

e) the settleability of the biological sludge and the ease of gravity liquids-solids separation.

Previous studies concerning petrochemical waste treatment have indicated the following ranges with respect to the parameters (Eckenfelder, et. al., 1968):

a)	organic loading (lbsBOD/day/lb MLVSS	0.10 - 3.0
b)	BOD removal as a function of the effluent concentration,	K range .00028-.0006

$$\frac{\text{BOD removed (mg/1)}}{\text{MLVSS conc(mg/1) x detention time (hrs)}} = \text{K (BOD of the effluent)}$$

c)	oxygen requirements, fraction of BOD removed	.40 - .70
d)	biological sludge production, fraction per day of MLVSS (aeration basin)	.22 - .60

It is apparent that the magnitude of these range of values requires an exact determination for each wastewater considered, especially due to the diverse nature of petrochemical wastes. Laboratory or pilot plant studies should therefore preceed actual design and construction.

It is important to recognize the response of treatment plant efficiency in terms of BOD and COD removal, and biological sludge settleability in terms of zone settling velocity and sludge volume index, to the applied organic loading. These responses are graphically illustrated in Figure VII-5.

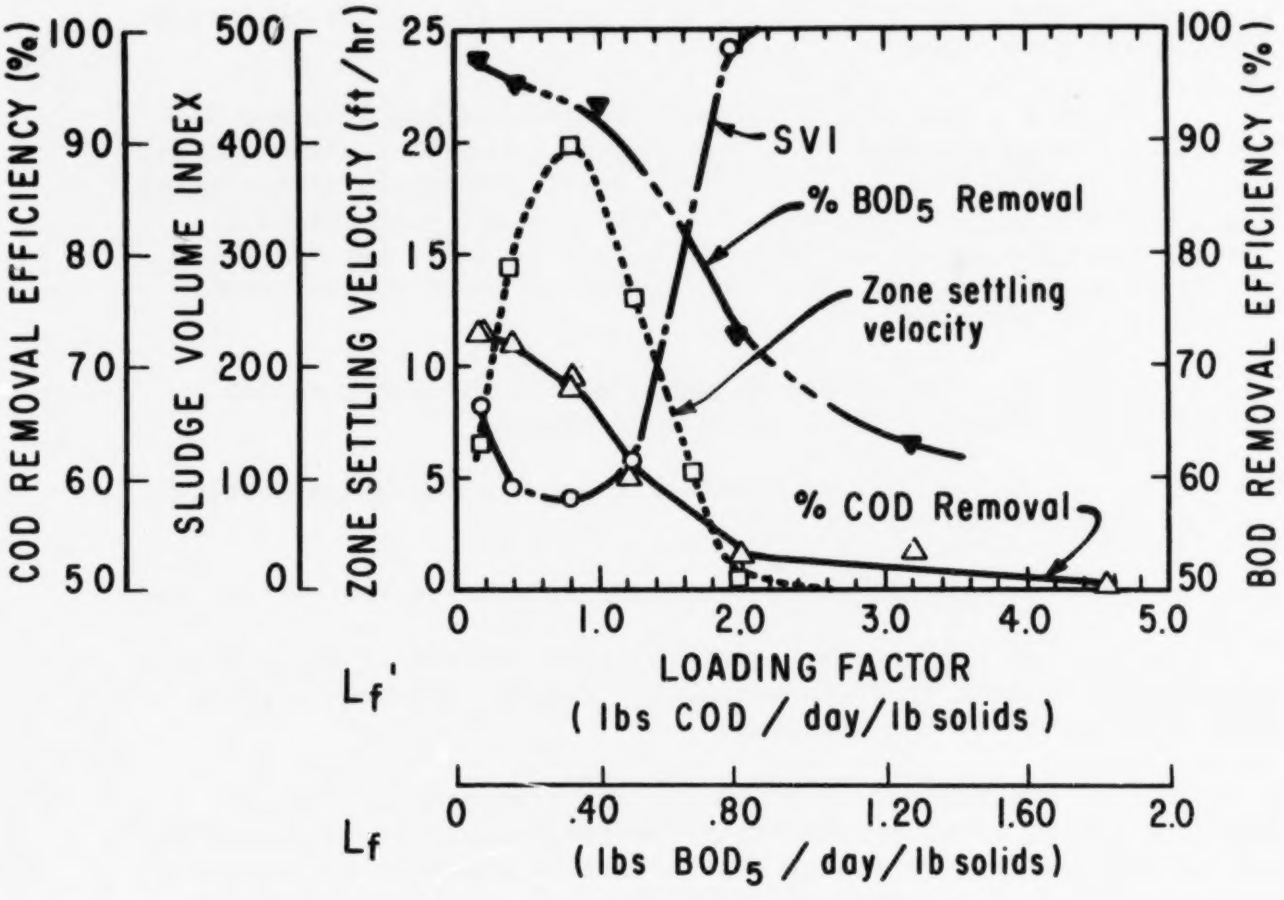


FIGURE VII-5
PARAMETER RESPONSE TO ORGANIC LOADING - PETROCHEMICAL WASTES
(Reference 38)

A wide range of applied organic loadings to activated sludge plants have been reported for petrochemical waste treatment. Extended aeration, a process where long detention periods allow oxidation of biological solids thus minimizing sludge disposal requirements, is characterized by organic loading values of 0.1 to 0.3 lbs BOD/day/lb MLSS. Conversely, loadings in excess of 1.0 lbs BOD/day/lb MLVSS are not uncommon for some high-rate activated sludge processes, although loading ranges of 0.2 to 0.7 are usually considered as optimal in the treatment of industrial wastes.

A summary of activated sludge plants treating petrochemical wastes, including information concerning the petrochemical products, applied loadings, nutrient requirements, and effluent quality are tabulated in Table VII-17. It is noted that the treatment efficiency in terms of COD removal is highly variable while maximum BOD removals are generally the same. It should be recognized that many organic compounds can be chemically oxidized while remaining resistant to biochemical degradation, therefore being registered as COD but not BOD. The difference between the measured COD and BOD values therefore indicates the magnitude of the non-biodegradable organic fraction in the wastewater. For example, 99 percent of the BOD was removed from a petrochemical wastewater containing morpholine and ethers, while the COD removal only ranged from 25 to 40 percent (Gloyna and Ford, 1966).

There are two categories of aeration systems utilized in activated sludge systems. One system uses compressed air which is sparged or diffused directly into the mixed liquor, while the other moves the mixed liquor, bringing it into contact with the air. These categories are known respectively as diffused air and mechanical aeration systems. The requirements of both systems can be summarized as follows:

a) to transfer oxygen from the gas phase to the liquid phase, insuring liquid dissolved oxygen;

b) to mix and disperse the dissolved oxygen throughout the aeration basin;

c) to mix and uniformly disperse the wastewater; and

d) to maintain the biological solids in suspension, allowing sufficient bacteria-wastewater contact and thus promote full utilization of the microbes.

Mechanical aeration systems are normally used in aeration basins treating industrial wastes because of lower installation and maintenance costs. These surface aerators are either pier-mounted or float-mounted. The impeller, shaft, and bearing design differ with the manufacturer, although the transfer mechanism

TABLE VII-17

ACTIVATED SLUDGE TREATMENT OF PETROCHEMICAL WASTES

Product and/or Process	Flow (MGD)	BOD			COD			Organic Loading $\left(\frac{\text{lb BOD}_5\text{/day}}{\text{lb MLSS}}\right)$	Nutrients Reqd.	Remarks	Ref
		In (mg/1)	Out (mg/1)	Rem (%)	In (mg/1)	Out (mg/1)	Rem (%)				
Refinery, Natural Gas Liquids, Chemical Specialties, Sanitary Sewage	4.87	90	20	78	200	90	55	0.1	None	Effl. phenol 0.05 Effl. oil 0.5 mg/1	117
Phthalic Anhydride, Phenol, Salicylic Acid, Rubber Chem., Aspirin, Phenacetin	2.54	45.7	6.1	86.7				0.031	None	Brush Aeration, treats trickling filter effluent, 55% sludge return	116
Refinery, Detergent Alkylate	2.45	345	50-100	71-85.5	855	150-200	76.6-82.5	0.08	PO_4	Phenols in = 160 mg/1 Sulfide in = 150 mg/1 Lab scale	42
Butadiene Maleic Acid	2.0	2,000	25	98.8	2,990	480	84	0.24	NH_3		26
Butadiene Alkylate	1.5	1,960	24	98.8	2,980	477	98.3				26
Butadiene, Maleic Anhydride Fumaric Acid, Tetrahydrophthalic, Anhydride, Butylene Isomers, Alkylate	1.5	1,960	24	98.8	2,980	51	84	0.24 (MLVSS)	NH_3	Surface aerators wastes contain: alcohols, maleic acid, fumaric acid, acetic acid, C_1-C_4 aldehydes, furfural, water soluble addition products	93

TABLE VII-17 (Continued)

ACTIVATED SLUDGE TREATMENT OF PETROCHEMICAL WASTES

Product and/or Process	Flow (MGD)	BOD			COD			Organic Loading $\left(\frac{\text{lb BOD}_5\text{/day}}{\text{lb MLSS}}\right)$	Nutrients Reqd.	Remarks	Ref
		In (mg/1)	Out (mg/1)	Rem (%)	In (mg/1)	Out (mg/1)	Rem (%)				
Ethylene Propylene, Benzene	1.44	600	90	85	700	105	85		None	Oily waters: C_4-C_{10} oils 90% phenol removal	102
Naphthalene, Butadiene, Phenol, Acrylonitrile, Soft Detergent Bases, Resins, Other Aromatics	0.43	500	60	85-90	600	90	80-85	1.5	NH_3 PO_4	Sour waters: Oil in = 500 mg/1 Phenol in = 65 mg/1 pH adjustment, preceeded by trickling filter, phenol removal = 99.9%	102
Phenol, 2, 4-D Aniline, Nitro-Benzene, Rubber Chem., Polyester Resins, Misc. Chem.	0.97	370	76	76.2				0.4	NH_3 PO_4	Accelator Pilot Plant Sewage added in ratio 1:600 once a week	85
Ethylene, Propylene, Butadiene, Benzene, Polyethylene, Fuel Oils	0.63	85	10	99	200	75	62.5			Quench waters, polyethylene and benzene wastes: preceeded by trickling filter, effl. phenol 0.01 ppm	104
Refining Processes	0 51-0.63	125	15-25	80-88			65-80	0.28-0.4	PO_4	Phenol removal 85-94%; Oil removal 75-85%; Effl. phenol 0.5 mg/1; Effl. oil 1-2 mg/1; Temp. - 30°C	66
Nylon	0.4	1,540	250	83.8							26
Petroleum Products	0.27	440	5	98.8	500	60	88			Phenol in = 25 ppm Phenol out - 1 ppm	26

TABLE VII-17 (Continued)

ACTIVATED SLUDGE TREATMENT OF PETROCHEMICAL WASTES

Product and/or Process	Flow (MGD)	BOD			COD			Organic Loading ($\frac{\text{lb BOD}_5\text{/day}}{\text{lb MLSS}}$)	Nutrients Reqd.	Remarks	Ref
		In (mg/l)	Out (mg/l)	Rem (%)	In (mg/l)	Out (mg/l)	Rem (%)				
Acrylic Fibers	0.252	2,260	118-226	90-95				0.4		Wastes contain acrylonitrile, dimethylamine, dimethylformamide, formic acid temp. 35-37°C return sludge 10-50% mechanical aeration	109
Acetone, Phenol p-Cresol, Ditert.-Butyl-p-Cresol, Dicumyl Peroxide	0.216	3,560-4,400	1,030-750	71-83				0.89-1.1		Waste phenol 600 ppm Waste BOD 7,500-8,000 Waste diluted w/ effl. or water; pilot plant	25
Resins-Formalin, Aminoplasts, Phenol-Formald., Epoxy Resins, Textile Aux.	0.2	890	444-266		50-70			0.8-1.2		Diffused-air; domestic waste added; trickling filter follows 100% recycle sludge	105
Ethylene and Propylene Oxides, Glycols, Morpholines, Ethylene-Diamines, Ethers, Piperazine	0.15	1,950	20	99	7,970-8,540	5,120-5,950	25-40	0.51	None	Lab Scale; extended aeration; high non-biodegradable fraction followed by stab. ponds	41
2, 4-D 2,4,5-T (Acid Wash Wastes)	0.1	1,670	125	92.5	2,500	500	80	0.78 (MLVSS)	NH_3 PO_4	1:1 mixture of acid wash streams diluted 9:1 prior to treatment to reduced chlorides, toxicity Lab Scale	40

TABLE VII-17 (Continued)

ACTIVATED SLUDGE TREATMENT OF PETROCHEMICAL WASTES

Product and/or Process	Flow (MGD)	BOD			COD			$\frac{\text{lb BOD}_5\text{/day}}{\text{lb MLSS}}$	Nutrients Reqd.	Remarks	Ref
		In (mg/1)	Out (mg/1)	Rem (%)	In (mg/1)	Out (mg/1)	Rem (%)				
Cracking, Isomerization of Butane and Naphthene, Alkylation, Benzene, Toluene, Alcohols, Ketones, Cresylic Acids		1,100	55-110	90-95				0.5		90-95% phenol removed; Lab Scale	21
Ethylene, Acetylene			20					0.23-0.33	PO_4	Effl. phenol 0.1 mg/1 Effl. oil 1 ppm	66
Nylon Manuf.-Adipic Acid Aaidonitricz Alk. Organics				95			85	1.0-3.0	PO_4 NH_3	NH_4 OH used as nutrient and neutralizing agent waste diluted 2:1	22 96

is the same. Vertical shaft units normally have a transfer capacity of 2.0 to 3.3 pounds oxygen per hour per horsepower under standard conditions (20°C, pure water, zero initial dissolved oxygen), and a power level of about 0.1 horsepower per 1,000 gallons of aeration basin required to keep solids in suspension, although this value is a function of tank geometry and aerator spacing.

Horizontal shaft aerators have also been used in the treatment of industrial wastes. These steel cage rotors can be adjusted by varying the speed of rotation and the paddle immersion depth.

Turbine aeration systems are commonly used when complete mixing is required and a deep basin is necessary. Compressed air is released through a sparge ring beneath an impeller close to the bottom of the aeration tank. An additional surface impeller is attached to the same shaft. Although the oxygen transfer efficiency is slightly lower than surface mechanical systems, these units have a better mixing ability.

Trickling Filter Processes

Trickling filters are commonly used in industrial waste treatment systems, primarily as "roughing devices" designed to level out and reduce organic loads to activated sludge or aerated lagoon processes. They have been used quite successfully in this manner although stringent effluent quality standards are rarely met when filters are used singularly.

Trickling filters employ microbial films attached to rock or synthetic media to remove organic materials from the wastewater solution. Most filter processes incorporate recirculation of the treated effluent in order to increase the filter efficiency. The recirculated effluent dilutes the raw wastewater, thereby reducing the organic concentration of the waste applied to the microbial slime. Recycle ratios as high as 40:1 have been required in the treatment of some petrochemical wastes because of their high initial concentration of dissolved organics.

Although the organic loading plays an important role in their performance, a trickling filter with a definite depth and media size can undergo loading changes with very little effect on the effluent quality until the optimum loading is reached (Anon., API, Biological Treatment of Petroleum Refinery Wastes). Once this loading is surpassed, the excess organics merely pass through the filter, causing a rapid deterioration in effluent quality.

Although BOD removals obtained in trickling filters are usually less than that removed in the activated sludge process, toxic effects are not as pronounced or perpetual. When the active biological slime in contact with the toxic substances dies and sloughs away, it is simply replaced by the underlying growth attached to the media. Additionally, filter design and operation is relatively simple.

Rock and synthetic media are used to provide the necessary surface area for the growth and proliferation of microorganisms. Media specifications consider both maximum surface area for bacterial growth, and maximum voids area for optimum wastewater passage and ventilation. It has been determined that two-inch to four-inch diameter rocks offer the best stone media for filters which are usually six to 12 feet in depth. Plastic media are used primarily in filters which have higher hydraulic and organic loadings than rock filters. The original plastic filter media, polystyrene, was subject to chemical attack by solvent spills, etc., although the advent of polyethylene filter media has eliminated this problem. Because of the controlled void space, no plugging or ventilation problems have been encountered in synthetic media type filters employing depths up to 40 feet.

The recorded treatment of various chemical and petrochemical wastes using trickling filters is tabulated in Table VII-18. Although BOD removals as high as 98 percent were observed, the usual treatment efficiency ranged from 75 percent to 90 percent removal of five-day BOD.

A variety of wastes have been successfully treated, as shown in Table VII-18. Excellent phenol reductions ranging from 73 to 96 percent have been obtained at phenol loadings of 0.17 to 18.0 lbs phenol/day/1,000 ft^3 (Anon., API, Biological Treatment of Petroleum Refinery Wastes). The phenol content of synthetic resin wastes was reduced from 4,500 mg/l to 1.5 mg/l by treatment using two filters in series containing plastic media (Chipperfield, 1967). In addition to phenol, this waste also contained large quantities of formaldehyde, fatty acids, phthalic acid, and maleic acid and an overall reduction in BOD of 95 percent was observed. Another plastic media filter was used to treat acrylic fiber wastes containing both acrylonitrile and large quantities of zinc (Sadow, 1960). Effective treatment was obtained at the reported zinc levels, the metal being extracellularly adsorbed by the microorganisms in the filter slime. Other data, as indicated in Table VII-18, indicate that trickling filters can be used effectively to completely or partially remove many compounds commonly found in petrochemical wastewaters.

Aerated Lagoons

Aerated lagoons are basins six to 12 feet in depth where oxygen is supplied by mechanical or diffused aeration units. There are two general types of aerated lagoons, the aerobic lagoon and the facultative lagoon. In the aerobic lagoon, all biological solids are kept in suspension while sludge settling and consequent anaerobic decomposition are characteristic of the facultative

TABLE VII-18

TRICKLING FILTER TREATMENT OF PETROCHEMICAL WASTES

Product and/or Process	Flow (MGD)	BOD			COD			Organic Loading $\left(\frac{\text{lb BOD}_5/\text{day}}{1{,}000\ \text{ft}^3}\right)$	Deficient Nutrients	Remarks	Ref
		In (mg/1)	Out (mg/1)	Rem (%)	In (mg/1)	Out (mg/1)	Rem (%)				
Phenol, Salicylic Acid, Rubber Chem.,	2.59	190	58	69.5				40.5	None	Rock Media, recirc. ratio 2.84:1	116
Aspirin, Phenacetin, Phthalic Anhydride	2.59	58	34	41.5				11.8	None	Rock Media, treats effluent from above filter, effluent to act. sludge	
Plastics, Amines, Enzymes	1.06	1,960	37	98.1	2,660	230	91.5			2 filters, followed	26
Ethylene, Propylene, Butadiene, Benzene, Polyethylene, Fuel Oil	0.63	170	85	50	400	200	50	89	None	Plastic filter media followed by act. sludge phenol removal = 95% influent diluted 2:1 w/cooling water	104
Aliphatic Acids, Esters, Alcohols, Aromatics, Amines, Inorganic Salts	0.57-0.86	1,100-2,300	23-470	57-99				42.1-82 (Both filters combined)	None	pH adjusted prior to treatment; 2 filters in series; Recycle on 1st state is 14-21:1	106
Ethylene, Propylene, Butadiene, Benzene, Naphthalene, Phenol, Acrylonitrile, Soft. Detergent Bases, Resins	0.43	1,300			1,500	450	60-70	140	NH_3 PO_4	Sour Waters, Rock Media	102

TABLE VII-18 (Continued)

TRICKLING FILTER TREATMENT OF PETROCHEMICAL WASTES

Product and/or Process	Flow (MGD)	BOD			COD			Organic Loading $\left(\frac{\text{lb BOD}_5\text{/day}}{1{,}000\ \text{ft}^3}\right)$	Deficient Nutrients	Remarks	Ref
		In (mg/1)	Out (mg/1)	Rem (%)	In (mg/1)	Out (mg/1)	Rem (%)				
Pentaerythritoc Waste contains Formaldehyde, Sodium Formate, Methanol, Pentaerthritol	0.118	5,080-5,800	225-232*	95-96*				1st stage 65	NH_3 PO_4 Yes	2 filters in series followed by act. sludge; recycle 40-1 on prim. filter, 13-1 second	24
Resins-Formaum, Aminoplasts,	0.17			82.6				11.7	None	Both filters treat act. sludge effluent,	105
Phenol-Formal, Epoxy Resins, Textile Aus.	0.03			89.3				14.6	None	Blast furnace slag media Waste contains phenol, formaldehyde, methanol	
Acrylic Fibers	0.32		13	30-70		49	30-70	50 84	NH_3 PO_4	Waste contains: acrylonitrile and zinc plastic filter media	101
Synthetic Resins-Phenol, Formaldehyde, Fatty Acids, Phthalic Acid, Maleic Acid, Glycerol, Pentaerythritol, H.C. Solvents				95-98				1st stage 85 (as Phenol) 2nd stage 11.6-18.2 gpd/ft^3		Plastic media, 2-stage treatment; Influent: Phenol = 4,500 mg/1 Formaldehyde = 2,000 mg/1 Fatty acids = 800 mg/1 Phthalic and maleic acids = 1,000 mg/1 Eff. phenol = 1.5 mg/1	18

TABLE VII-18 (Continued)

TRICKLING FILTER TREATMENT OF PETROCHEMICAL WASTES

Product and/or Process	Flow (MGD)	BOD			COD			Organic Loading lb BOD_5/day ($\frac{}{1,000\ ft^3}$)	Deficient Nutrients	Remarks	Ref
		In (mg/1)	Out (mg/1)	Rem (%)	In (mg/1)	Out (mg/1)	Rem (%)				
Waste contains Acrylates, Acetone, Inhibitor oils, Alcohols, Esters, H_2SO_4 Organic Acids								51-79	None None	Original loading was lower value, loading increased w/o any adverse effects 15,000 lb BOD_5 removal per day	16

* Entire Treatment System

aerated lagoon. Since there are no secondary sedimentation and sludge recycle provisions associated with aerated lagoons, the suspended solids concentration (MLSS) in the basin is quite low. The exact solids concentration will reach an equilibrium level which depends upon the organic concentration of the waste, the synthesis sludge rate coefficients, and the amount of power imparted to the basin liquid. Equilibrium MLSS levels in aerated lagoons normally range from 80 mg/l to 250 mg/l.

Aerated lagoon basins normally involve excavation - earthern embankment type construction - although concrete structures are sometimes used. Earthern tank bottoms and side-slopes should be lined with materials such as vinyl, granite, lean concrete, or rip-rap to insure erosion protection.

High levels of treatment are not normally obtained in the aerated lagoons because of the BOD and COD associated with the effluent suspended solids and the relatively small number of active biological solids in contact with the wastewater. Aerated lagoons are particularly sensitive to transient organic loadings, toxic substances, and temperature changes. In one instance, a pilot plant aerated lagoon treating a mixed chemical waste reduced 87 percent of the BOD in the summer while only a 23 percent removal was obtained during winter operating conditions (Ling, 1963).

Aerated lagoons are being used successfully as economical treatment devices, either as a process preceeding waste stabilization ponds or as an interim treatment process which can later be converted to an activated sludge unit by adding secondary clarification and recycle facilities.

A recently completed aerated lagoon - waste stabilization pond facility, for example, has proven to be quite successful in treating a refinery-petrochemical wastewater (Gloyna, Brady and Lyles, 1968). If the organic load increases, it is envisioned to convert the aerated lagoon to activated sludge.

A summary of reported data from the aerated lagoon treatment of petrochemical wastewater is given in Table VII-19.

Waste Stabilization Ponds

Waste stabilization ponds are wastewater treatment devices which depend on the natural aquatic processes of bacterial and algal symbiosis and have been used in the successful treatment of petrochemical wastes. Although ponds are often used to polish the effluent from other biological waste treatment processes, they have been used in some instances to treat entire plant wastes (Anon., API, Vol. III, 1958).

TABLE VII-19

AERATED LAGOON TREATMENT OF PETROCHEMICAL WASTES

Product and/or Process	Flow (MGD)	BOD			COD			Organic Loading $\frac{\text{lb BOD}_5}{\text{Acre}\cdot\text{day}}$	Nutrients Reqd.	Remarks	Ref
		In (mg/1)	Out (mg/1)	Rem (%)	In (mg/1)	Out (mg/1)	Rem (%)				
Refinery Butadiene, Butyl Rubber	19.1	225	100	55	610	350	43	4,630	PO_4	Followed by stab. pond temp = 32°C 30% COD is non-biodegradable Lab Scale	43
Refinery, Detergent Alkylate	2.45	345	50-100	71-85	855	150-200	77-83	6,300	PO_4	Influent phenols 160 mg/1 Influent sulfides 150 mg/1 Lab Scale	42
Cyclohexane, p-Xylene, Benzene, Paraffinic Naphtha, o-Xylene Gasoline Nylon Fibers	0.51	100	25	75				400		Surface aeration, waste is extensively pretreated. Followed by pond	69
Chemicals for Lubricating Oils	0.2	465	180	61	1,050	600	43				26

Functional waste stabilization ponds are normally categorized as "facultative," that is the upper layers of the pond are kept aerobic while anaerobic decomposition is prevalent in the lower layers.

Empirical equations which consider the BOD loading, temperature, and toxic substance effect on microorganisms have been developed and successfully used to design facultative waste stabilization ponds (Gloyna, 1966).

Anaerobic ponds are devoid of oxygen because of the high organic loads, normally above 200 to 500 lbs/day/acre. These units function best when there is a large biodegradable solid load. Although odors are a problem, it is an effective device in partially reducing the organic concentration of the wastewater prior to being discharged to subsequent biological treatment processes. Pretreatment by anaerobic ponds, for example, minimizes floating sludge problems which occur in facultative ponds during the summer months (Gloyna, 1966). Anaerobic ponds, however, are more pH and temperature sensitive than are facultative ponds.

The performance of pilot plant and prototype waste stabilization ponds in treating petrochemical wastes is shown in Table VII-20. The effluent BOD is a function of the surface loading, detention time, and environmental factors as well as the quantity of BOD associated with the suspended solid fraction (dead algal cells, debris, etc.). Although the effluent quality of waste stabilization ponds in terms of BOD is comparable to other unit processes, the COD reduction capability is often higher. This is attributable to the extended detention time which provides the microorganisms sufficient time to degrade the more refractory compounds, or those substances which exert a COD but little or no BOD_5. As a rule, oxidation ponds are more efficient in reducing oils and sulfide concentrations than they are in reducing phenols. One heavily loaded waste stabilization pond with a detention time of 1.25 days reduced oil from 68 to 43 mg/l, sulfide from 42 to five mg/l, while phenols decreased only from 42 to 40 mg/l (Anon., API, Biological Treatment of Petroleum Refinery Wastes). Another pond, with a detention time of 30 days, reduced oil from 150 to 0 mg/l, sulfides from 15 to 0 mg/l, while reducing phenols from 20 to seven mg/l.

The salient problems associated with waste stabilization ponds treating petrochemical wastes are twofold: (a) the adverse effect of emulsions and highly colored substances which prevent sunlight penetration and cause reduced photosynthesis and (b) the toxic effects of many compounds on the pond algae, upsetting the symbiotic algal-bacterial relationship. Dumps of waste containing hydrogen sulfide, sulfates, phenols, etc., can cause severe reductions in BOD removals. Excessive releases of sulfur-containing

TABLE VII-20

WASTE STABILIZATION POND TREATMENT OF PETROCHEMICAL WASTES

Product and/or Process	Flow (MGD)	BOD In (mg/1)	BOD Out (mg/1)	BOD Rem (%)	COD In (mg/1)	COD Out (mg/1)	COD Rem (%)	Organic Loading lb BOD_5 $\left(\frac{}{\text{Acre} \cdot \text{day}}\right)$	Nutrients Reqd.	Remarks	Ref
Refinery, Butadiene Butyl Rubber	19.1	100	50	50	350	200	43	Primary pond 91; Total ponds 46	None	Ponds in series after aerated lagoon Lab Scale	43
Resins, Alcohols, Amines, Esters, Styrene, Ethylene	5	500-1,000	400-700	20-60				96	None	Anaerobic	12
	5	400-700	25-50	88-96				164	None	Anaerobic	12
	5	25-50	5-30	40-90				5	None	Aerobic	12
Butane, Propane, Nat. Gas, Ethanol, Ethyl Chloride, Polyethylene, Ammonia, H_2SO_4	3.25	150	7-15	90-95	260			75	None	Facultative pond, 18 days detention Infl. $SO_4 = 650$ mg/1	118
Refinery, Detergent Alkylate	2.45	50-100	20-50	50-80	150-200	120	20-40	95	None	After Aerated Lagoon Or Act. Sludge Lab Scale	42
Plastics	1.69	686	186		1,681	590	65			Facultative Ponds	26
Ethylene and Propylene Oxides, Glycols, Morpholines, Ethylenediamines, Ethers, Piperazine	0.15	20			5,120-5,950	4,610-4,450	10-25	25	None	Lab Scale Facultative Ponds to remove some resid. COD. High non-biodegradable fraction. After activated sludge	41
Mixed Petrochemicals				95-99			75-96	100		Facultative ponds	119

compounds enhance the growth of colored bacteria and there is a concurrent reduction of green algae. Laboratory tests have indicated that when hydrogen sulfide content of the pond reaches five to 10 mg/l, the pond will cease to function (Gloyna, Brady and Lyles, 1968). The concentrations of selected petrochemical inhibitors toxic to algae were noted in the previous chapter, Table VI-8

Miscellaneous Biological Treatment Processes

Two more promising treatment processes, Table VII-21, are cooling towers and sand filters. The use of cooling towers is schematically illustrated in Figure VII-6. In addition to reducing the temperature of the cooling water by evaporation, cooling towers also provide for the introduction of dissolved oxygen to the wastewater, enhancing aerobic bio-oxidation of organics within the tower. A cooling tower system treating one refinery waste removes 3,800 lbs of BOD per day and reduces the phenol concentration from 12 mg/l to 0.09 mg/l. A similar system reduces the phenolic concentration from three mg/l to 0.06 mg/l. In both cases, low-solids process wastes are used as make-up water.

Periodic blowdowns are necessary to keep the dissolved and suspended solids in the cooling water at required levels. The BOD of this blowdown will still be high because of the pressure of suspended biological sloughing, so that subsequent treatment of blow-down is required. Backwashing of the process coolers is often employed to prevent clogging or fouling by biological materials. Generally, only a few problems associated with additional equipment corrosion have been observed while using this system.

Although cooling water treatment has been used exclusively in refinery complexes, such systems undoubtedly have application for reuse of specific petrochemical wastewaters.

Similar to the spray irrigation practices which have been used in treating industrial wastewaters, is the percolating sand filter which has been used in pilot plant investigations using a percolating sand filter as a biological treatment device and has shown some promise (Dickerson and Laffey, 1959). Microorganisms which are capable of degrading the particular wastes are developed in the sand-soil medium. Intermittent dosing then provides the contact time necessary for adequate biodegradation.

Multiple Biological Treatment Schemes

Many petrochemical wastes are treated by multiple component biological treatment systems (Gloyna and Malina, 1963). The complexity of most petrochemical wastes and the associated effluent qualities requirements often circumvent single-stage biological

TABLE VII-21

MISCELLANEOUS BIOLOGICAL TREATMENT PROCESSES FOR FOR PETROCHEMICAL WASTES

Treatment Process	Product and/or Process	Waste Characteristics	Remarks	Ref
Cooling Towers	Refining Process	Low Solids Process Wastes	BOD removal = 80% weight basis 30-50% concentration basis Phenol removal = 98-99% concentration basis	77
Sand Filter (w/Biol. Growth)	Acetone, Phenol, p-Cresol, di-tert-butyl-p-cresol, Dicumyl Peroxide	BOD 3,200 mg/l Volatile acids 860-2,150 mg/l Phenol 50 mg/l 50 gpm flow	Pilot plant - 6' deep 92-97% BOD removed 100% volatile acids removed load = 70,000 gal/acre · day	24

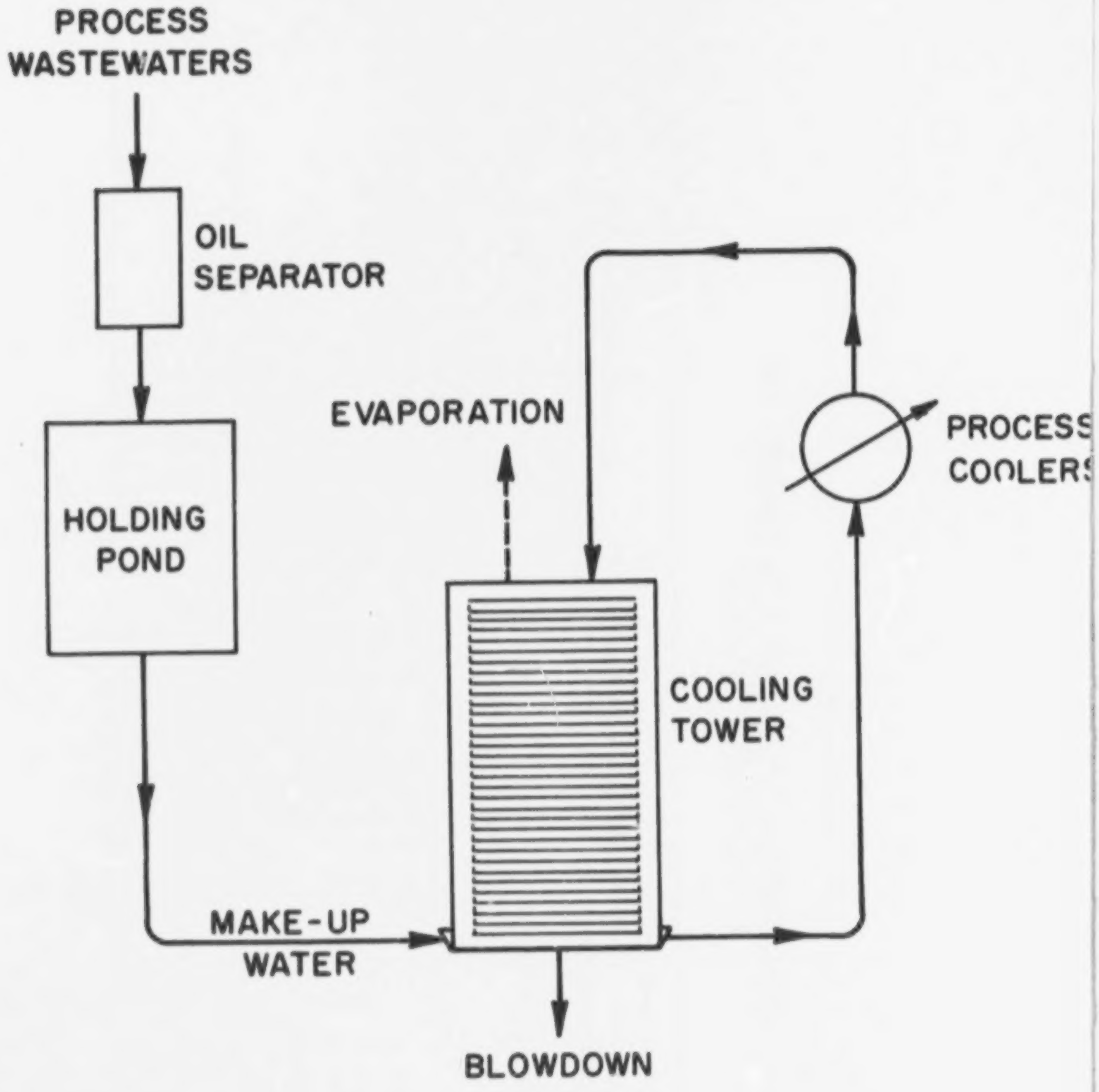

PROCESS WASTEWATERS
OIL SEPARATOR
HOLDING POND
EVAPORATION
PROCESS COOLERS
COOLING TOWER
MAKE-UP WATER
BLOWDOWN

FIGURE VII-6

BIOLOGICAL TREATMENT IN A COOLING TOWER - SCHEMATIC DIAGRAM treatment. Various combinations of biological processes are therefore used to treat petrochemical wastes, depending on wastewater characteristics, treatability, economic considerations, and effluent quality requirements. Applications of multiple biological treatment systems are tabulated in Table VII-22. The organic removal data indicated include that BOD and COD chemically or physically removed in pretreatment processes. The data as presented in this table show that activated sludge, trickling filters, and waste stabilization ponds are the most common processes used in multiple treatment systems.

OTHER METHODS OF DISPOSAL

There are several methods which are often employed for the disposal of petrochemical solid and liquid wastes. The following methods are discussed herein:

a) dilution,

b) discharge into municipal sewerage systems,

c) deep well disposal,

d) ocean disposal,

e) submerged combustion, and

f) incineration.

The process selected from those mentioned above will depend on the volume and nature of the wastewater, capital and operating cost considerations, and plant location.

Dilution

This form of waste disposal is becoming less and less popular with regulatory authorities and the trend is toward the mandatory primary and secondary treatment of all wastewaters. However, certain petrochemical plants are allowed to discharge their wastewaters to receiving bodies of water without treatment providing

a) sufficient receiving water is available as a diluent,

b) there are no toxic or refractory compounds in the waste stream, and

c) the assimilative and recovery capacity of the receiving water based on the pollutional input is adequate.

TABLE VII-22

MULTIPLE BIOLOGICAL TREATMENT SYSTEMS FOR PETROCHEMICAL WASTES

Products and/or Process	Biological Treatment		3rd Stage (If Applicable)	Removal		Ref
	1st Stage	2nd Stage		BOD (%)	COD (%)	
Butadiene, Butyl Rubber, Refinery	Aerated Lagoon	Facultative Pond		>78	>67	44
Cyclohexane, p-Xylene, Benzene, Paraffinic Naphtha, o-Xylene, Gasoline, Nylon	Aerated Lagoon	Facultative Pond		>75		69
Detergent Alkylate, Refinery	Aerated Lagoon	Facultative Pond		95	86	42
Refinery-Chemical	Aerated	Stabilization		95	88	54
Ethylene and Propylene Oxides, Glycols, Morpholines, Ethylenediamines, Ethers, Piperazine	Activated Sludge	Facultative Pond		>99	35-65	41
Polyester Fibers	Activated Sludge	Stabilization Pond		97.5		26

TABLE VII-22 (Continued)

MULTIPLE BIOLOGICAL TREATMENT SYSTEMS
FOR PETROCHEMICAL WASTES

Product and/or Process	Biological Treatment		3rd Stage (If Applicable)	Removal		Ref
	1st Stage	2nd Stage		BOD (%)	COD (%)	
Refinery, Natural Gas Liquids, Chemical Specialties	Activated Sludge	Stabilization Pond		86	70	117
Synthetic Resins	Activated Sludge	Trickling Filters		>99		105
Resins, Alcohols, Amines, Esters, Styrene, Ethylene	Anaerobic Lagoon	Anaerobic Lagoon	Aerobic Lagoon	97-99		11
Ethylene, Propylene, Butadiene, Benzene, Gasoline, Polyethylene, Fuel Oils	Trickling Filters	Activated Sludge		>98	>93	104
Phenol, Salicylic Acid, Aspirin, Phenacetin, Phthalic Anhydride, Rubber Chemicals	Trickling Filters	Activated Sludge		98		116
Refinery	Trickling Filter	Activated Sludge	Stabilization Pond			52

TABLE VI-22 (Continued)

MULTIPLE BIOLOGICAL TREATMENT SYSTEMS FOR PETROCHEMICAL WASTES

Products and/or Process	Biological Treatment		3rd Stage (If Applicable)	Removal		Ref
	1st Stage	2nd Stage		BOD (%)	COD (%)	
Plastics, Amines	Trickling Filter	Stabilization Pond		>98	91.5	26
Pentaerythritol	Trickling Filter	Trickling Filter	Activated Sludge	95-96		24
Synthetic Resins	Trickling Filter	Trickling Filter		95-98		18
Aliphatic Acids, Alcohols, Esters, Aromatics, Amines	Trickling Filter	Trickling Filter	Stabilization Pond			106

Rapid wastewater-diluent mixing is required, and this often is accomplished by the use of jets or diffusers.

The quality and use of the receiving water often dictates direct discharge practices. For example, regulatory authorities often permit the discharge of spent caustic wastes directly into salt lakes, brackish streams, and estuaries (McRae, 1959).

Discharge Into Municipal Sewerage Systems

Joint industrial-municipal treatment has proved to be workable in treating petrochemical wastewaters, especially where small plants are located near large metropolitan areas (Elkin, 1959). The ability to successfully co-treat, however, has certain constraints. Discharges of petrochemical wastes containing high concentrations of toxic materials to municipal sewerage systems may upset the treatment facility. Therefore, pre-treatment may be required before many industries are allowed to connect with the municipal system. For example, the wastewaters from two Los Angeles, California synthetic rubber plants must be pre-treated to remove oil, rubber particulates, and other suspended and floating matter prior to discharge (Martin and Rostenbach, 1953).

Although joint industrial-municipal wastewater collection and treatment is feasible in certain cases, it has generally been found that individual treatment has both economic and political advantages, particularly where large volumes of petrochemical wastewater are involved. It is for this reason that less than three percent of the chemical-petrochemical plants in the United States discharged their wastes to municipal sewers in 1963 (U. S. Bureau of Census, 1963) with no future increases expected in this percentage.

Deep Well Disposal

Subsurface disposal of liquid wastes is not a new concept as the oil and gas producers have been using this method for disposing of oil field brines for half a century. However, only recently have the process industries realized the applicability of deep well injection for disposing of concentrated and relatively untreatable waste streams. Since much of the land surface is underlain by great aquifers containing salt water or brines, these formations offer convenient and safe repositories for these wastes, preventing pollution of usable surface and subsurface water supplies.

In 1967, 30 permits for industrial disposal wells had been issued in Texas, 26 of which were for industries producing petroleum-based products (Fink, 1967). The national total number of industrial waste disposal wells in 1966 was estimated at 71 (Warner, 1966). This does not include those wells in which oil field brines are injected, either for the purpose of disposal or to increase formation pressures in oil-bearing strata.

Disposal wells used for the subsurface injection of petrochemical wastewaters are listed in Table VII-23. Injection rates range from a few gallons per minute to over 600 gallons per minute. The depth at which these wastes are discharged vary from a few hundred feet to as deep as 12,000 feet, with most systems injecting a wellhead pressure of 2,000 pounds per square inch or less (Gloyna and Ford, 1967). The more common formations into which wastes are injected include unconsolidated sands, sandstone, limestones, and dolomites (Warner, 1966). It is necessary to determine the permeability of the formation by drilling test wells. Additionally, the compatability of the wastewater with the formation water must be established. The dangers of contaminating potable water-bearing formations can be assessed by studying the overlying and underlying strata and locating unplugged wells in the contiguous area.

Most of the petrochemical wastewaters noted in Table VII-23 must be pretreated prior to injection. The characteristics of the wastewater and the nature of the receiving formation dictate the exact pre-treatment requirements. Conditions that require surface treatment and those facilities commonly employed are summarized in Table VII-24.

The pH adjustment of wastewaters is often of primary importance when considering the performance of the injection well. Neutralization is often required, but adjustments to the acid or base range are sometime advantageous. For example, the acidification of a petrochemical wastewater prior to injection in a limestone formation resulted in higher "injection" rates at lower wellhead pressures (Lockett, 1967). In another case, rigid pH control was required, as a wastewater containing acetic acid and its chlorinated derivatives formed polymeric tars at pH values greater than five, while precipitates were formed at a pH of less than four (Vier, 1967).

Ocean Outfall

The direct discharge of petrochemical wastes into the ocean is feasible when locations permit. Most liquid wastes flow through outfall pipelines, the distance of discharge from shore depending on the nature of the wastewater, the ocean currents, and shoreline use. Barge disposal is another method of conveying wastewaters to the ocean for disposal, but this practice has been abused and requires strict control. Chlorinated hydrocarbons have been barged to a point 100 miles from the Gulf Coast and discharged over a 30-mile wide area (Hood, et. al., 1958).

A review of the literature indicates that many different unit processes are applicable in treating the diverse wastewaters discharged from the petrochemical industy. The number of process installations reported in 1965 by the Petroleum and Chemical industries, each interrelated with petrochemical production, is listed

TABLE VII-23

PETROCHEMICAL WASTE DISPOSAL BY DEEP WELL INJECTION - TYPICAL INSTALLATIONS

Type Waste	Flow (gpm)	Depth (ft)	Injection Pressure (psia)	Formation	Required Pretreatment	Ref
Acrylonitrile and Detergent Manuf. Wastes: COD = 17,500 mg/l; Nitrites = 300 mg/l; pH = 5.4, SO_4 = 10,000 mg/l	650	7,203	Up to 2,000	Sat. Brine, Miocene Sands	Neutralization; Settling and Equalization in Pond; Coagulation pH Adjustment and Clarification; Gravity Sand Filters	102
10-15% NaCl; Diss. Metal Salts; Trace Organics; pH 7.5-8.5	500-600	4 wells:	200	Unconsolidated Brine Sands	Oil Separation; Settling; Pressure Leaf Filtration; Diatomite Filtration	63 23
Refinery and Petrochem. Cooling Water Blow-down Boiler Blow-down, Process Waters	500	1,200	75	Sandstone		55
Petrochem. Waste Organic Nitrogen Nitrites COD = 20,000 ppm pH = 12 Uranium 238	400	6,700	400	Sands	Neutralization, Precipitation - Sedimentation, Filtration	55
Phenolic Waste: COD = 12,000 ppm; 850 ppm Phenol; 150 ppm Oil; pH 10.8	300	6,330	1,000	Sat. Brine, Miocene Sands	Neutralization with H_2SO_4; Clarifier, Pressure Sand Filter	102
Aromatics Phenols 1,000-2,000 ppm COD 10,000 ppm pH 10.7	300	6,100	1,000	Miocene Sands		55

TABLE VII-23 (Continued)

PETROCHEMICAL WASTE DISPOSAL BY DEEP WELL INJECTION - TYPICAL INSTALLATIONS

Type Waste	Flow (gpm)	Depth (ft)	Injection Pressure (psia)	Formation	Required Pretreatment	Ref
0.3% Acetic Acid and Chlorinated Derivatives	204	3,700	2,000	Miocene Brine Sand	Cool to 150^{o}F. Adjust pH to 4.0-5.0, Settling Coal Filter; Cartridge Filter for Solids $>10\mu$	111 70
Terephthalic Acid Manuf. Cooling and Boiler Blow-down, Process Wastes Containing Organic Acids, H. C., inorganics	150	5,600		Sands	Settling, Filtration	55
Nylon, Ammonia, Olefins, Polyolefins, Refinery, Butadiene, Styrene, Synthetic Rubber 1	Small-96	5,802	800-1,100	Limestone	Conventional Waste Treatment, 0.3% by Volume of Acid, Added Before Injection	73
Cuprous Ammonium Acetate from Butadiene Pond; Caustic Waste from Ethylene Prod., Caustic and Phenols from Refinery	85	>4,000	1,500-2,000		Equalization, Settling	104
Refinery Cooling and Boiler Blowdown, Process Wastes, Brines	50	5,000	600	Sandstone	Settling and Storage	55
Ammonia Prod.	45	1,000	225	Sandstone	API Separator	55

TABLE VII-23 (Continued)

PETROCHEMICAL WASTE DISPOSAL BY DEEP WELL INJECTION - TYPICAL INSTALLATIONS

Type Waste	Flow (gpm)	Depth (ft)	Injection Pressure (psia)	Formation	Required Pretreatment	Ref
Hydrochloric Acid	40	1,200	14.7	Sandstone	None	55
Detergent Product 32% HCl Benzene Chlorinated HC	35	3,400		Miocene Sands	Dilution with Equal Volume Fresh Water	55
Spent Alkylation Acid- 90% H_2SO_4; 7% Oil; 3% H_2O	~ 1	5,100				64
Filtrates and Distillates from Chloromycetin Manuf: BOD_{20} = 45,000 ppm; pH 3.5; Diss. Solids = 50,000 ppm		1,400		Saturated Brine, Sand		1
Saturated NaCl, Conc. Ca-Mg, Liquors, Phenols, Chloro-Phenols, Bis-Phenols, Methocel, Weak Caustic Washes		3,000		Limestone	Suspended Solids Removed	93

TABLE VII-24

POLLUTANTS REQUIRING SURFACE TREATMENT PRIOR TO DEEP WELL INJECTION

Wastewater Characteristics	Surface Treatment
1. Suspended solids	settling, centrifugation, or filtration *
2. Dissolved gases	degasification by purging, air stripping, etc.
3. Colloidal matter, turbidity	coagulation and precipitation, followed by sedimentation and/or filtration
4. Ions which precipitate on contact with formation waters	possible pH adjustment, coagulation and precipitation followed by sedimentation and/or filtration
5. Oils and oil-like polymers	skimming devices, oil separators
6. Corrosive character	neutralization or installation of corrosion-resistant piping and appurtenances
7. Biological activity and growth	chlorination, filtration

* Filter aids may be required.

in Table VII-25. The data indicate that lagoons or stabilization basins are the most commonly used processes, probably based on the economics as related to current effluent quality requirements.

Submerged Combustion

Submerged combustion is the burning of a gaseous fuel in a specially designed burner with the burner chamber submerged in the wastewater. This device has been used successfully in totally or partially evaporating waste streams, concentrating any dissolved solids, either which have reuse value or which are easier to dispose of than large volumes of the liquid waste.

A submerged combustion unit reduced 75 percent of the volume of a nylon waste stream, the remainder of which was mixed with other process streams and treated biologically (Remy, E. D. and Lauria, D. T., 1958). A polymeric waste stream containing suspended synthetic rubber particles, organic solvents, inorganic salts, and synthetic detergents was not amenable to biological treatment and consequently treated by submerged combustion (Weyermuller, G. and Davidson, J., 1958). This waste stream was evaporated to about 10 percent of its original waste volume with the resulting slurry emptied to a drying bed. Volatile organic compounds in the polymeric waste, such as alcohols and amines, were oxidized or burned so that no odors were detected in the surrounding area.

Incineration of Liquid Wastes

Incineration of combustible and partially combustible liquid wastes is often a feasible method of disposing of concentrated process streams. The properly designed incineration system considers time, temperature, and turbulence. Sufficient residence time should be provided to permit complete oxidation of the organic material, the temperature should be high enough for the reaction to proceed, and the system should be sufficiently turbulent to insure that the oxygen in the air is contacted with the dissolved organic material (Ross, R. D., August 1967).

Although incineration is a practical means of handling a wide variety of effluents, it should be evaluated only in the light of the total pollution problem, particularly air pollution.

TABLE VII-25

TYPES OF WASTE TREATMENT USED IN THE PETROLEUM AND CHEMICAL INDUSTRIES

Secondary Treatment Process*	Number of Installations Reported
Activated sludge	12
Anaerobic digestion	9
Biological filtration	6
Centrifuging	4
Chemical coagulation	13
Chemical oxidation or reduction	12
Distillation and stripping	43
Extraction	4
Fermentation	1
Filtration	15
Flotation (air)	26
Incineration	2
Stabilization ponds	59
Wet oxidation	5

Waste Treatment Method*	Number of Mentions	Percent
Biological oxidation	105	9
Chemical oxidation or reduction	62	5
Flotation	76	6
Incineration	71	6
Lagooning or settling	468	39
Neutralization	307	25
Other	122	10
TOTAL	1,211	100

*More than one treatment process may be in use at each plant.

REFERENCES - CHAPTER VII

1. Adinoff, J., "Disposal of Organic Chemical Wastes to Underground Formations," *Ind. Wastes*, v. 1, n. 1, p. 4944 (Sept.-Oct. 1955).

2. Anderson, R. E. and Hansen, R. D., "Phenol Sorption on Ion Exchange Resins," *Ind. & Engr. Chemistry*, v. 47, p. 71 (1955).

3. Anon., *Biological Treatment of Petroleum Refinery Wastes*, American Petrol. Inst., New York, N. Y.

4. Anon., "How Shell Cut Pollution in Rhinelands," *The Oil and Gas J.*, v. 58, p. 93 (Oct. 31, 1960).

5. Anon., *Manual on Disposal of Refinery Wastes*, Vol. I, "Waste Water Containing Oil," American Petrol. Inst., New York, N. Y. (1953).

6. Anon., *Manual on Disposal of Refinery Wastes*, Vol. III, "Chemical Wastes," American Petrol. Inst., New York, N. Y. (1958).

7. Anon., *Manual on Disposal of Refinery Wastes*, Vol. IV, "Sampling and Analysis of Waste Water," American Petrol. Inst., New York, N. Y. (1958).

8. Anon., "Petrochemical Handbook 1967," *Hydrocarbon Processing*, v. 46, p. 11 (1967).

9. Anon., "Selected Process Flow Sheets for Petrochemicals," *The Oil and Gas J.*, v. 36, n. 36, p. 107 (1964).

10. Anon., "Tables Show How to Treat Petrochemical Wastes," *Petro/Chem. Engineer*, p. 25 (May 1967).

11. Anon.,"Union Carbide Puts Corporate Muscle in Pollution Fight," *The Oil and Gas J.*, v. 64, n. 50, p. 132 (1966).

12. Anon., Water in Industry, National Assoc. of Manufacturers and Chamber of Commerce of the U. S., New York and Washington, D. C. (1965).

13. Beychok, M. R., Aqueous Wastes from Petroleum and Petrochemical Plants, John Wiley & Sons, London (1967).

14. Brunner, C. A. and Stephan, D. G., "Foam Fractionation," Ind. & Engr. Chemistry, v. 57, n. 5, p. 40 (May 1965).

15. Brunsmann, J. J., et. al., "Improved Oil Separation in Gravity Separators," J. WPCF, v. 34, n. 1, p. 44 (Jan. 1962).

16. Brush, A. E. and Wheeler, W. W., "Treatment of a Petrochemical Waste on a Trickling Filter," Proc. 2nd Ind. Water & Waste Conf., Texas Water Poll. Control Assoc., Austin, Texas, p. 171 (1962).

17. Carbone, W. E., et. al., "Commercial Dephenolization of Ammoniadal Liquors with Centrifugal Extractors," Proc. 13th Ind. Waste Conf., Purdue Univ., p. 87 (1958).

18. Chipperfield, P. N. J., "Performance of Plastic Filter Media in Industrial and Domestic Waste Treatment," J. WPCF, v. 39, n. 11, p. 1860 (Nov. 1967).

19. Clark, F. E., "Industrial Re-Use of Wastewater," Ind. & Engr. Chemistry, v. 54, n. 2, p. 18 (Feb. 1962).

20. Cochran, L. G. and Bess, F. D., "Waste Monitoring by Gas Chromatography," J. WPCF, v. 38, n. 12, p. 2002 (Dec. 1966).

21 Coe, R. C., "Bench Scale Method for Treating Waste by Activated Sludge," Petrol. Proc., v. 7, p. 1128 (Aug. 1952).

22. Dean, B. T., "Nylon Waste Treatment," J. WPCF, v. 33, n. 8, p. 864 (Aug. 1961).

23. DeRopp, H. W., "Chemical Waste Disposal at Victoria, Texas, Plan of the DuPont Co.," Sew. and Ind. Wastes, v. 23, n. 2, p. 194 (1951).

24. Dickerson, B. W., Campbell, C. J. and Stankard, M., "Further Operating Experiences on Biological Purification of Formaldehyde Wastes," Proc. 9th Ind. Waste Conf., Purdue Univ., p. 331 (1954).

25. Dickerson, B. W. and Laffey, W. T., "Pilot Plant Studies of Phenolic Wastes from Petrochemical Operations," Proc. 14th Ind. Waste Conf., Purdue Univ., p. 780 (1959).

26. Eckenfelder, W. W., Jr., "Effluent Quality and Treatment Economics for Industrial Wastewater," Rept. to the F.W.P.C.A., Washington, D. C. (1967).

27. Eckenfelder, W. W., Jr., Industrial Water Pollution Control, McGraw-Hill Book Co., New York, N. Y. (1966).

28. Eckenfelder, W. W., Jr., et. al., Unpublished Rept. (1968).

29. Eckenfelder, W. W., Jr. and Ford, D. L., Unpublished Rept. (1968).

30. Eckenfelder, W. W., Jr., Ford, D. L. and Burleson, N. K., Unpublished Rept. (July 1968).

31. Eckenfelder, W. W., Jr., Kleffman, R. and Walker, J., "Some Theoretical Aspects of Solvent Stripping and Aeration of Industrial Wastes, Proc. 11th Ind. Waste Conf., Purdue Univ., p. 14 (1956).

32. Eisenhauer, H. R., "Oxidation of Phenolic Wastes," J. WPCF, v. 36, n. 9, p. 1116 (Sept. 1964).

33. Elkin, H. G., "Condensates, Quenches, and Wash Waters as Petrochemical Waste Sources," Petrochemical Wastes, v. 31, n. 7, p. 836 (July 1959).

34. Englebrecht, R. S. and Ewing, B. B., "Treatment of Petrochemical Wastes by Activated Sludge Process," Proc. 2nd Ind. Water and Waste Conf., Texas Water Poll. Control Assoc., Austin, Texas, p. 149 (1962).

35. Federgreen, N. and Weinberger, A. J., "Methyl Styrene-A Case Study in Spent Acid Catalyst Treatment," Ind. & Engr. Chemistry, v. 49, p. 46 (1957).

36. Fink, B. E., "State Regulation of Subsurface Waste Disposal in Texas," Proc. 7th Ind. Water and Waste Conf., Texas WPCA (1967).

37. Ford, D. L., "Kinetics of Aerobic Oxidation in the Thermophyllic Range," Master's Thesis, The Univ. of Texas, Austin (1964).

38. Ford, D. L., "The Effect of Process Variables on Sludge Floc Formation and Settling Characteristics," Doctoral Dissertation, The Univ. of Texas, Austin (1960).

39. Ford, D. L. and Eckenfelder, W. W., Jr., Unpublished Rept. (March 1968).

40. Ford, D. L. and Gloyna, E. F., Unpublished Rept. (Jan. 1967).

41. Ford, D. L. and Gloyna, E. F., Unpublished Rept. (Feb. 1967).

42. Ford, D. L. and Gloyna, E. F., Unpublished Rept. (May 1967).

43. Ford, D. L. and Gloyna, E. F., Unpublished Rept. (July 1967).

44. Ford, D. L. and Gloyna, E. F., Unpublished Rept. (June 1968).

45. Ford, D. L., Gloyna, E. F. and Eckenfelder, W. W., Jr., Unpublished Rept. (June 1968).

46. Garrett, J. T., "Multipurpose Incineration," Ind. Wastes, v. 2 n. 5, p. 111 (1957).

47. Garrett, J. T., "Tars, Spent Catalysts, and Complexes as Petrochemical Waste," Sew. and Ind. Wastes, v. 31, n. 7, p. 841 (July 1959).

48. Gaudy, A. F., Jr., Englebrecht, R. S. and Turner, B. G., "Stripping Kinetics of Volatile Components of Petrochemical Wastes, J. WPCF, v. 33, n. 4, p. 382 (April 1961).

49. Giebler, G., "Treatment of Wastewaters of the Pesticide Industry," Vom Wasser, v. 25, p. 197 (1958).

50. Gill, J. M., et. al., "Submarine Disposal System for Treated Chemical Wastes," J. WPCF, v. 32, p. 858 (August 1960).

51. Gill, J. M., Huguet, J. H. and Pearson, E. A., "Submarine Disposal System of Treated Chemical Wastes," J. WPCF, v. 32, n. 8, p. 858 (Sept. 1960).

52. Gilliam, A. S., "Biological Disposal of Refinery Wastes," Proc. 14th Ind. Waste Conf., Purdue Univ., p. 145 (1959).

53. Gloyna, E. F., Waste Stabilization Pond Design, Seminar "Water Pollution Control in the Chemical Industry," Sponsored by the Manufacturing Chemists Assoc., Austin, Texas (1966).

54. Gloyna, E. F., Brady, S. O. and Lyles, H., "Use of Aerated Lagoons and Ponds in Refinery and Chemical Waste Treatment," Presented at 41st Annual WPCF Conf., Chicago, Ill. (Sept. 22, 1968).

55. Gloyna, E. F. and Ford, D. L., "Injection of Wastewaters into Disposal Wells," Unpublished Rept. (1966).

56. Gloyna, E. F., Ford, D. L. and Burleson, N. K., Unpublished Rept. (March 1968).

57. Gloyna, E. F. and Malina, J. R., "Petrochemical Wastes Effect on Water," Ind. Water & Wastes, pt. 1, Sept.-Oct. 1962, pt. 2, Nov.-Dec. 1962, pt. 3, Jan.-Feb. 1963, pt. 4, March-April 1963.

58. Gossom, W. J. and Stevens, J. I., "The Near Ultimate Disposal of Refinery Wastes," Tech. Paper 65-42. Rocky Mountain Regional Meeting, Natl Petrol. Refiners Inst., Casper, Wyoming (1965).

59. Green, R. V. and Moses, D. V., "Destructive Catalytic Oxidation of Aqueous Waste Materials," Sew. and Ind. Wastes, v. 24, n. 3, p. 288 (1952).

60. Harkness, N. and Jenkins, S. H., "Chemical and Biological Oxidation of Styrene and Koprene,: J. Inst. of Sew. Purif., pt. 2, p. 216 (1958).

61. Hart, W. B., "Flocculation as a Treatment for Petroleum Refinery Wastes," Ind. & Engr. Chemistry, v. 49, n. 5, p. 77A (1957).

62. Heller, A. M., et. al., "Some Factors in Selection of a Phenol Recovery Process," Proc. 12th Ind. Waste Conf., Purdue Univ., p. 103 (1957).

63. Henkel, H. O., "Deep Well Disposal of Chemical Waste Water," Proc. of the 5th Annual Sanitary and Water Resources Engr. Conf., Vanderbilt Univ., Tech. Rept. 9, p. 26 (1966).

64. Holland, H. R. and Clark, F. R., "A Disposal Well for Spent Sulphuric Acid from Alkylating Iso-Butane and Butylenes," Proc. 19th Ind. Waste Conf., Purdue Univ., v. 49, n. 1, p. 195 (1964).

65. Hood, D. W., Stevenson, B. and Jeffrey, L. M., "Deep Sea Disposal of Industrial Wastes," Ind. & Engr. Chemistry, v. 50, n. 6, p. 885 (1958).

66. Huber, L., "Disposal of Effluents from Petroleum Refineries and Petrochemical Plants," Proc. 22nd Ind. Waste Conf., Purdue Univ. (1967).

67. Hyde, A. C., "Chemical Plant Waste Treatment by Ten Methods," J. WPCF, v. 37, n. 11, p. 1486 (Nov. 1965).

68. Karger, B. L. and Rogers, L. B., "Foam Fractionation of Organic Compounds," Anal. Chemistry, v. 33, n. 9, p. 1165 (August 1961).

69. Klippel, R. W., Report on Pollution Control Planning for the Guayama Petrochemical Complex, Phillips Petrol. Co., Bartlesville, Oklahoma (1966).

70. Klotzman, M. and Vier, B., "Celanese Pumps Wastes into Disposal Wells," The Oil and Gas J., v. 64, n. 15, p. 84 (1966).

71. Lewis, W. L. and Martin, W. C., "Remove Phenols from Waste Waters," Hydrocarbon Processing, v. 46, n. 2, p. 131 (Feb. 1967).

72. Ling, J. T., "Pilot Study of Treating Chemical Wastes with Aerated Lagoon," J. WPCF, v. 35, n. 8, p. 963 (August 1963).

73. Lockett, D. E., "Subsurface Disposal of Industrial Waste Waters," Presented at Southwestern Petrol. Short Course, Dept. of Petrol. Engr., Texas Tech College, Lubbock, Texas (April 1967).

74. Ludzack, F. J. and Ettinger, M. B., "Chemical Structures Resistant to Aerobic Biochemical Stabilization," J. WPCF, v. 32, n. 11, p. 1173 (Nov. 1960).

75. Ludzack, F. J., Scheffer, R. B. and Bloomhuff, R. N., "Experimental Treatment of Organic Cyanides by Conventional Processes," J. WPCF, v. 33, n. 5, p. 492 (May 1961).

76. Marks, D. R., "Operation and Problems of a Chemical Waste Incinerator," Proc. of the 5th Annual Sanitary and Water Resources Engr. Conf., Vanderbilt Univ., Tech. Rept. 9, p. 99 (1966).

77. Martin, A. E. and Rostenbach, R. E., "Industrial Waste Treatment and Disposal," Ind. & Engr. Chemistry, v. 45, n. 12, p. 2680 (Dec. 1953).

78. McKinney, R. E., American Petrol. Inst., Division of Refining, Biological Treatment of Petrol. Refinery Wastes, Chapter 2, New York, N. Y. (1963).

79. McKinney, R. E., "Biological Treatment Systems for Refinery Wastes," J. WPCF, v. 39, n. 3, p. 345 (1967).

80. McGauhey, P. H. and Klein, S. A., "Removal of ABS from Sewage," Public Works, v. 92, n. 5, p. 101 (May 1961).

81. McRae, A. D., "Disposal of Alkaline Wastes in the Petrochemical Industry," Sew. and Ind. Wastes, v. 31, n. 6, p. 712 (July 1959).

82. Meinhold, T. and Mandele, A., "Organo-metallic Plant Waste Purer Than River Waste," Chem. Processing, v. 23, p. 41 (1960).

83. Mencher, S. K., "Minimizing Waste in the Petrochemical Industry," Chem. Engr. Progress, v. 63, n. 10, p. 80 (Oct. 1967).

84. Mills, E. J. and Stack, V. T., "Biological Oxidation of Synthetic Organic Chemicals," Proc. 8th Ind. Waste Conf., Purdue Univ. p. 492 (1953).

85. Mills, R. E., "Development of Design Criteria for Biological Treatment of an Industrial Effluent Containing 2,4-D Waste Water," Proc. 14th Ind. Waste Conf., Purdue Univ., p. 340 (1959).

86. Morris, J. C. and Weber, W., Jr., Adsorption of Biochemically Resistant Materials From Solution. 2., AWTR-16, F.W.P.C.A., Cincinnati, Ohio (March 1966).

87. Nagy, C. K., "The Construction and Operation of an Incinerator for Chemical Plant Wastes," Proc. 12th Ind. Waste Conf., Purdue Univ., v. 42, n. 3, p. 177 (1958).

88. Niegowski, S. J., "Destruction of Phenols by Oxidation with Ozone," Ind. & Engr. Chemistry, v. 45, p. 632 (1953).

89. Pahren, H. R. and Bloodgood, D. E., "Biological Oxidation of Several Vinyl Compounds," J. WPCF, v. 33, n. 3, p. 233 (May 1961).

90. Phillips, C., Jr., "Treatment of Refinery Emulsions and Chemical Wastes," Ind. & Engr. Chemistry, v. 46, p. 300 (1954).

91. Popov, M. A., "Use of Ozone for the Final Treatment of Effluents from an Oil Refinery," Gigiena i Sanit., v. 25, n. 5, p. 92 (1960).

92. Prather, B. V., "Will Air Flotation Remove the Chemical Oxygen Demand of Refinery Waste Water?" Petroleum Refiner, v. 40, p. 177 (May 1961).

93. Pruessner, R. D. and Mancini, J., "Extended Aeration Activated Sludge Treatment of Petrochemical Waste at the Houston Plant of Petro-Tex Chemical Corporation," Proc. 21st Ind. Waste Conf., Purdue Univ., v. 50, n. 2, p. 591 (1966).

94. Reid, G. W., and Libby, R. W., "Phenolic Waste Treatment Studies," Proc. 12th Ind. Waste Conf., Purdue Univ., p. 250 (1957).

95. Reinbald, H., "Graphical Solutions Given to Oil-Water Separation Rates," Petroleum Refiner, v. 39, n. 12, p. 180 (1960).

96. Remy, E. D. and Lauria, D. T., "Disposal of Nylon Wastes," Proc. 13th Ind. Waste Conf., Purdue Univ., v. 43, n. 3, p. 596 (1958).

97. Rice, J. K., "Eliminate Waste Water Discharge," Petro/Chem Engineer, p. 21 (Oct. 1966).

98. Rolich, G. A., "Applications of Air Flotation to Refinery Waste Waters," Ind. & Engr. Chemistry, v. 46, p. 304 (1954).

99. Ruggles, W. C., "Basic Petrochemical Processes as Wastes Sources," Sew. and Ind. Wastes, v. 31, n. 3, p. 274 (March 1959).

100. Ryckmann, D. W. and Sawyer, C. N., "Anionic Synthetic Detergents and Water Supply Problems," J. AWWA, v. 49, n. 4, p. 480 (April 1957).

101. Sadow, R. D., "The Treatment of Zefran Fiber Wastes," Proc. 15th Ind. Waste Conf., Purdue Univ., p. 395 (1960).

102. Sadow, R. D., "Waste Treatment at a Large Petrochemical Plant," J. WPCF, v. 38, n. 3, p. 428 (March 1968).

103. Schindler, H., "Disposal of Refinery Waste Water Containing Water-Soluble Sulfonates," Petroleum Refiner, v. 28, n. 10, p. 152 (Oct. 1949).

104. Shannon, E. S., "Handling and Treating Petrochemical Plant Wastes: A Case History," Water & Sew. Works, v. 111, n. 5, p. 240 (1964).

105. Singleton, K. G., "Biological Treatment of Waste Water from Synthetic Resin Manufacture," Proc. 21st Ind. Waste Conf., Purdue Univ., p. 62 (1966).

106. Steen, J. H., Majewski, F. M. and Iezzi, T., "Waste Treatment at a Large Chemical Manufacturing Plant," Sew. and Ind. Wastes, v. 28, p. 866 (July 1956).

107. Stein, K. C., et. al., "Oxidation of Hydrocarbons on Simple Oxide Catalysts," Air Poll. Control Assoc., v. 10, n. 4, p. 275 (August 1960).

108. Talbot, J. S. and Beardon, J., "The Deep Well Method of Industrial Waste Disposal," Chem. Engr. Progress, v. 60 (1964).

109. Taylor, E. F., et. al., "Orlon Manufacturing Wastes Treatment," J. WPCF, v. 33, p. 1076 (Oct. 1961).

110. Tyler, R. G., et. al., "The Ozonation of Cyanide Wastes," Sew. and Ind. Wastes, v. 23, n. 9, p. 1150 (Sept. 1951).

111. Vier, B. B., "Celanese Deep Well Disposal Practices," Proc. 7th Ind. Water and Waste Conf., Texas WPCA (1967).

112. Vrablick, E. R., "An Evaluation of Circular Gravity Type Separation and Dissolved-Air Flotation for Treating Oil Refinery Waste Water," Proc. 12th Ind. Waste Conf., Purdue Univ., p. 72 (1957).

13. Walker, R. F., "Disposal of Industrial Wastes at Maitland, Ontario, Works of DuPont of Canada," Proc. 13th Ind. Waste Conf., Purdue Univ., p. 720 (1958).

114. Warner, D. L., "Deep Industrial Waste Injection Wells in the United States, A Summary of Pertinent Data," Report to the F.W.P.C.A., Cincinnati, Ohio (1966).

115. Weisman, W. I., "Applications of Submerged Combustion in Industrial Waste Treatment," Proc. 8th Ind. Waste Conf., Purdue Univ., p. 363 (1953).

116. Wilson, I. S., "The Treatment of Chemical Wastes," Waste Treatment, Isaac, P.C.G., ed., Pergamon Press, London, p. 206 (1960).

117. Word, J. C., Wright, M. V. and Klippel, R. W., paper entitled "Treating Complex Petroleum Wastes at Borger, Texas," all are of Phillips Petrol. Co.

118. Weyermuller, G. and Davidson, J. A., "Submerged Combustion Prevents Polymer-Waste Problem," Chemical Processing (Feb. 1958).

BLANK PAGE

CHAPTER VIII

ECONOMIC ASPECTS OF PETROCHEMICAL WASTE TREATMENT

Economics play an important and sometimes critical role in dictating the level of treatment petrochemical wastewaters receive. The major economic factors include

a) the capital cost of a treatment process required to produce a defined quality level of effluent and the operating costs associated with the selected treatment process,

b) the returns to the petrochemical industry resulting from the treatment of its wastewaters in terms of product recovery and water reuse, and

c) the in-plant modifications required to render a treatment process feasible or less costly.

A discussion of these and related factors as well as treatment cost data obtained from public and private sources are included herein.

THE COST OF WASTE TREATMENT

There are many approaches in predicting the treatment costs required to reduce petrochemical pollutants to the acceptable level. Attempts to relate capital costs to production units, wastewater flow, BOD, or other parameters have proved quite successful when certain industrial wastewaters are considered. However, the diverse nature of the petrochemical industry and the limited number of wastewater treatment facilities specifically designed for treating its wastewaters has made it difficult to establish cost function relationships which can be applied throughout the industry.

Most cost information available in the literature includes the entire waste treatment facility containing an infinite number of physical, chemical, and biological treatment process combinations. The statistical correlation of these costs with the aforementioned process parameters is poor, and there is consequently no basis for translating this information from one plant to another within the industry. A more effective approach for estimating the capital cost of a treatment facility is to calculate the unit costs of each process within the treatment system and add a given percentage of the total to include piping, pumping and related appurtenances, engineering, and contingencies. The bases for evaluating the capital and operating costs for many of the unit processes used in the treatment of petrochemical wastewaters are tabulated in Table VIII-1.

It is recognized that there are many variables that affect these cost relationships which are not considered herein. Some of these factors include

a) geographical location,

b) climatic conditions,

c) fluctuations in area labor and material costs,

d) land cost factors, and

e) overdesign considerations.

Cognizant of these constraints, a series of capital cost-waste flow relationships are presented. These graphs, Figures VIII-1 to VIII-16 represent costs based on 1968 construction costs (ENR 1,030). These relationships were developed from reported costs of unit processes included in chemical, refinery, petrochemical, and in some cases, municipal waste treatment systems. A generalized estimate thereby can be formulated which summarizes individual process costs and adds 35 to 45 percent of the sub-total to include related appurtenances and engineering. It is apparent that this approach is a general one, but based on the information available, it provides a means of estimating capital costs of plants treating petrochemical wastewaters.

Primary Treatment

The capital cost relationships developed for equalization tanks and neutralization facilities are shown in Figures VIII-1 and VIII-2. Similar information derived from published literature for gravity oil separators is described in Figure VIII-3. It is recognized that many factors, including the plant layout and nature of the wastewater, dictate the number and size of separators. The capital cost relationships for primary clarification facilities are shown in Figure VIII-4. Considering overflow rate and detention time as the bases for design, this cost function can be applied to both industrial and municipal waste.

Biological Treatment Processes

Attempts to correlate the capital cost of complete treatment systems to hydraulic and organic loadings have generally been unsuccessful due to the diverse nature of the industry.

TABLE VIII-1

SUGGESTED BASIS FOR COSTING UNIT PROCESSES

Type of Treatment	Design Basis	Construction Cost Basis	Operational Cost Basis
Pre- or Primary Treatment:			
Equalization	Volume	Cost/Volume	-
Neutralization	Waste Flow	Cost/Waste Flow	Acidity or Alkalinity
Oil Separation	Waste Flow-Overflow Rate	Cost/Waste Flow	-
Sedimentation	Overflow Rate	Cost/Surface Area	-
Biological Treatment:			
Waste Stabilization Ponds	Waste Flow-Surface Loading	Cost/Surface Area	-
Aerated Lagoons	Waste Flow-Organic Loading	Cost/Volume	-
Activated Sludge (Aeration tanks)	Waste Flow-Organic Loading	Cost/Volume	-
*Mechanical Surface (Aeration equipment)	Total HP	Cost/Volume	-
Secondary Clarifier	Overflow Rate	Cost/Surface Area	
Trickling Filter	Waste Flow-Organic Loading	Cost/Filter Volume	-

TABLE VIII-1 (Continued)

SUGGESTED BASIS FOR COSTING UNIT PROCESSES

Type of Treatment	Design Basis	Construction Cost Basis	Operational Cost Basis
Tertiary Treatment:			
Ion Exchange	Waste Flow	Cost/Waste Flow	-
Carbon Adsorption	Waste Flow	Cost/Waste Flow	-
Miscellaneous Processes:			
Gas Stripping	Waste Flow	Cost/Waste Flow	Air or Stream Usage
Coagulation	Waste Flow	Cost/Waste Flow	Chemical Requirements
Sludge Handling and Disposal:			
Thickening	Mass Loading	Cost/Thickener Volume	-
Flotation Thickening	Air/Solids Ratio-Overflow Rate	Cost/Surface Area	-
Vacuum Filtration	Filter Loading	Cost/Area of Filter	-
Centrifugation	Waste Flow and Solids Loading	Cost/Waste Flow	HP

TABLE VIII-1 (Continued)

SUGGESTED BASIS FOR COSTING UNIT PROCESSES

Type of Treatment	Design Basis	Construction Cost Basis	Operational Cost Basis
Ultimate Disposal:			
Deep Well Injection - Surface Treatment	Waste Flow	Cost/Waste Flow	-
Deep Well Injection	Waste Flow-Depth	Cost/Waste Flow	-
Incineration	Waste Flow-Heat Content	Cost/Waste Flow	-

* As Used in Aerated Lagoons and Activated Sludge

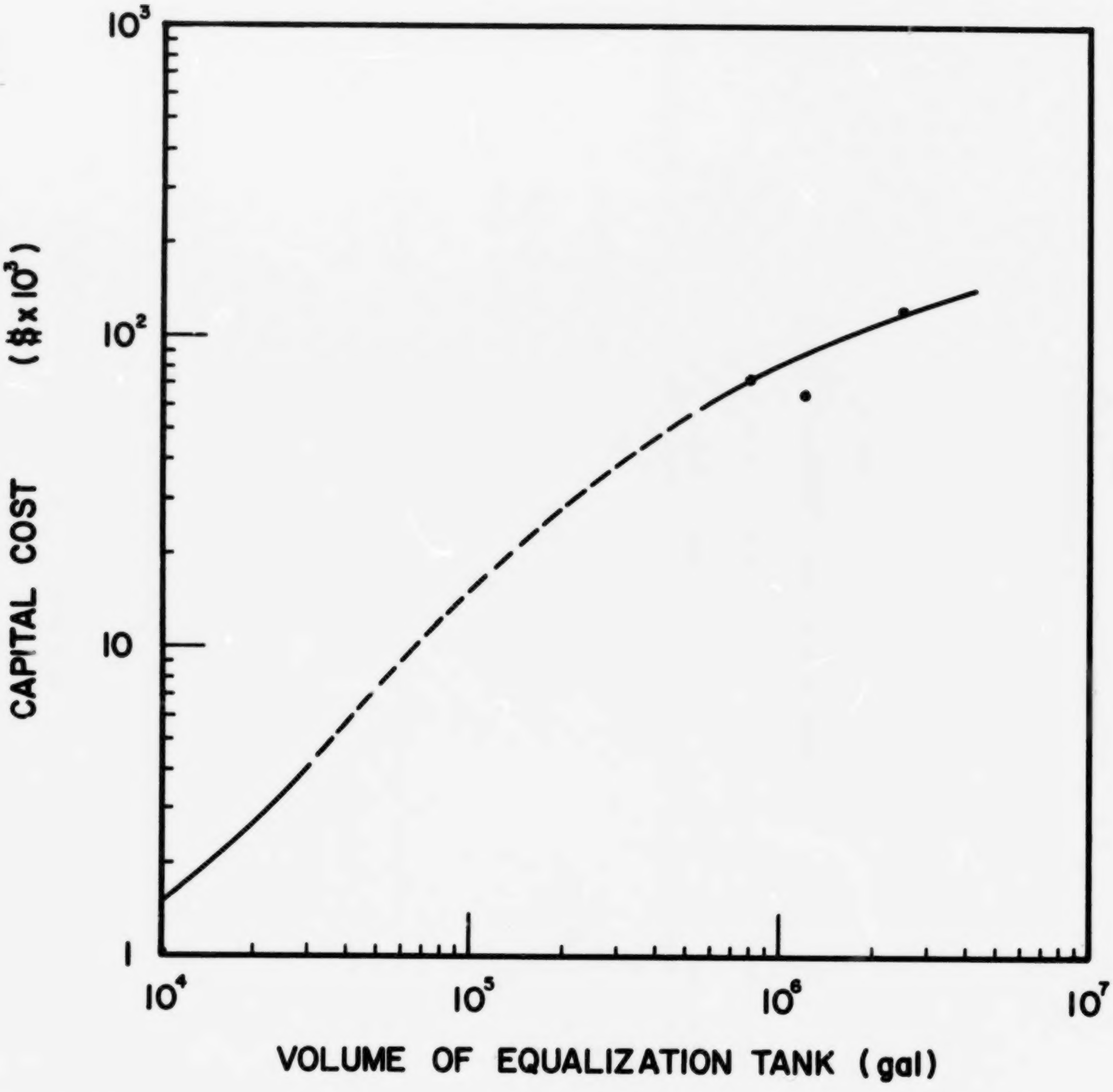


FIGURE VIII-1
CAPITAL COST RELATION - EQUALIZATION
(Reference 4)

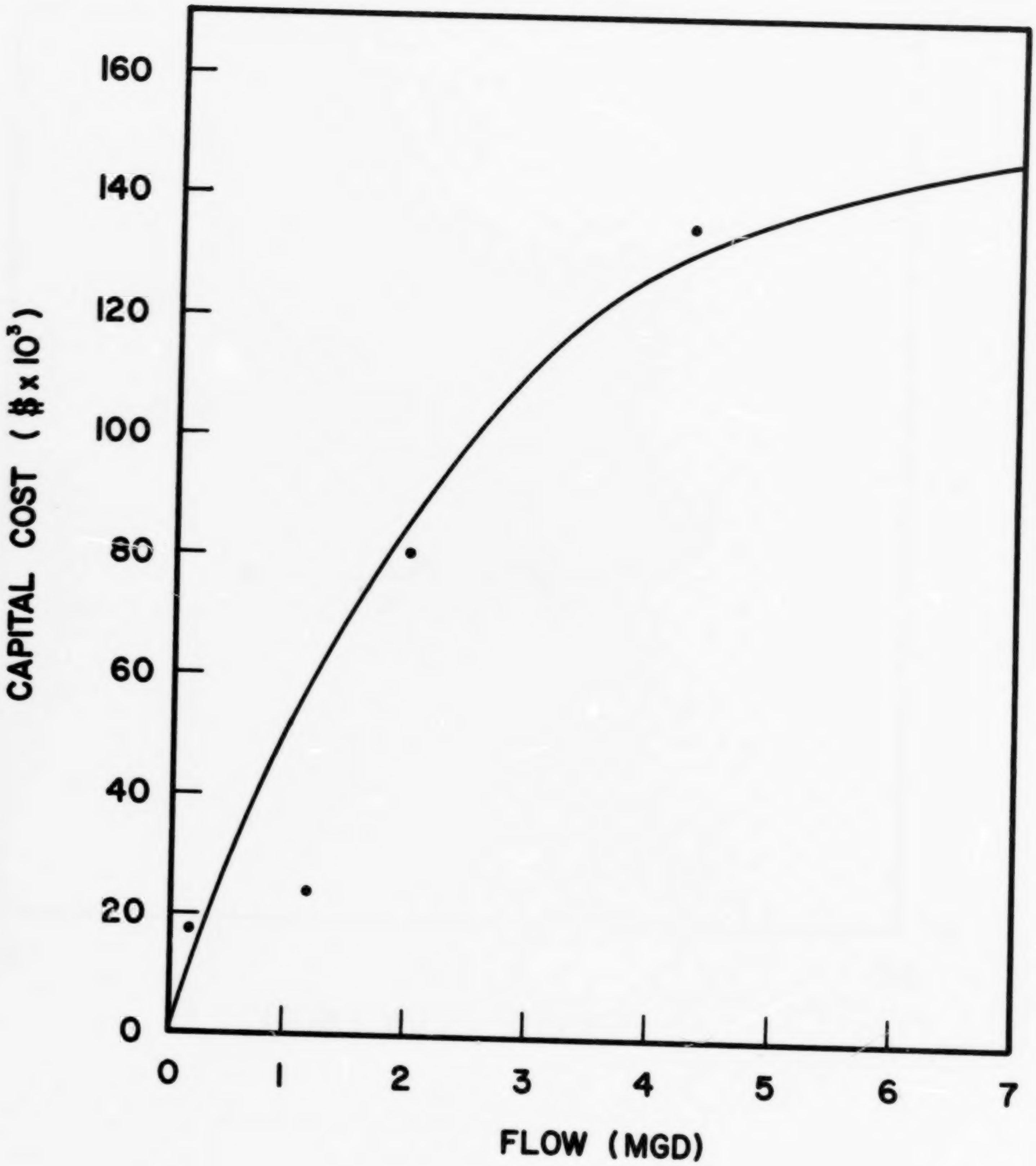


FIGURE VIII-2

CAPITAL COST RELATIONSHIP - NEUTRALIZATION

(Reference 4)

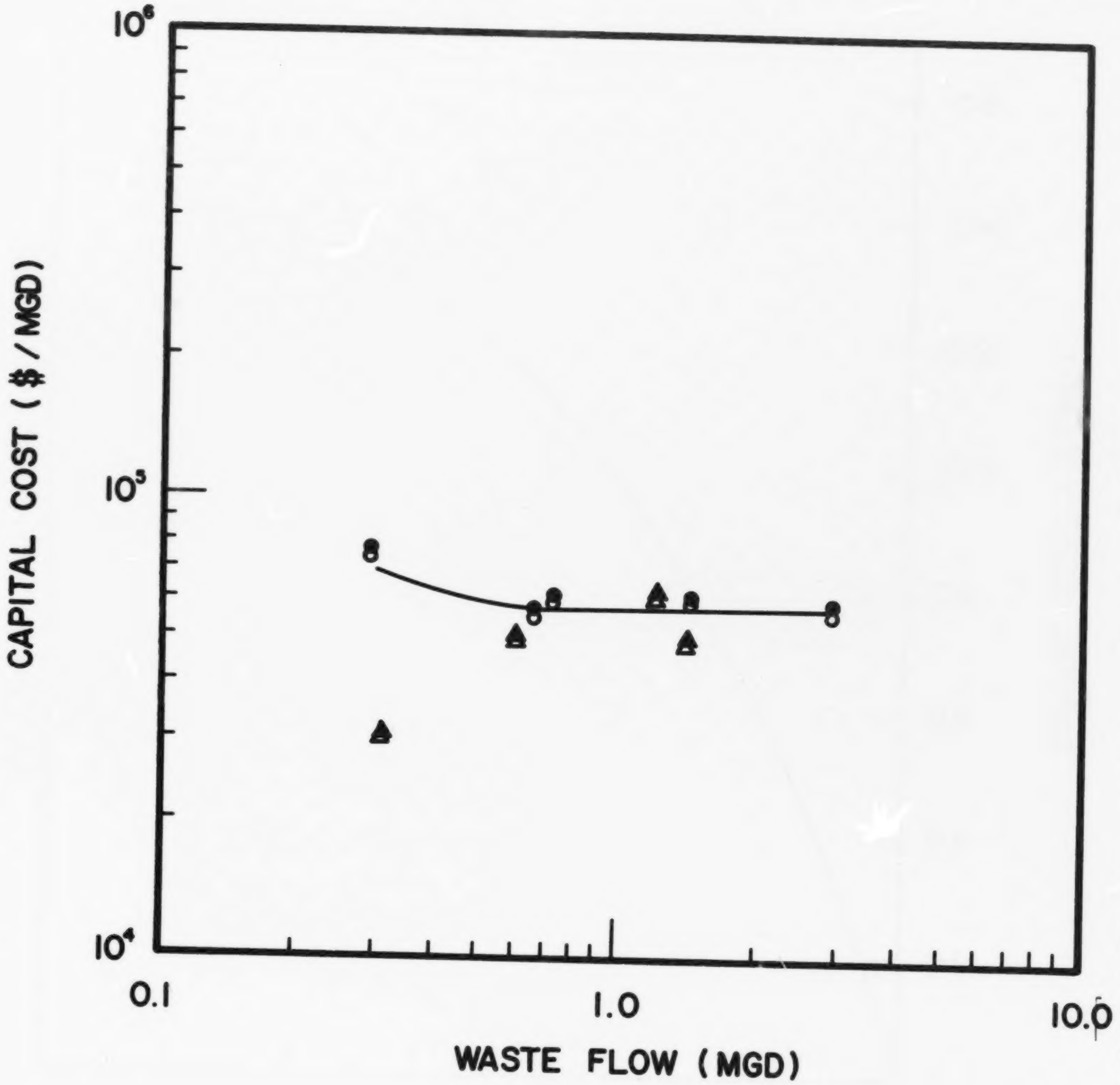


FIGURE VIII-3
CAPITAL COST RELATIONSHIP - OIL SEPARATION
(Reference 2)

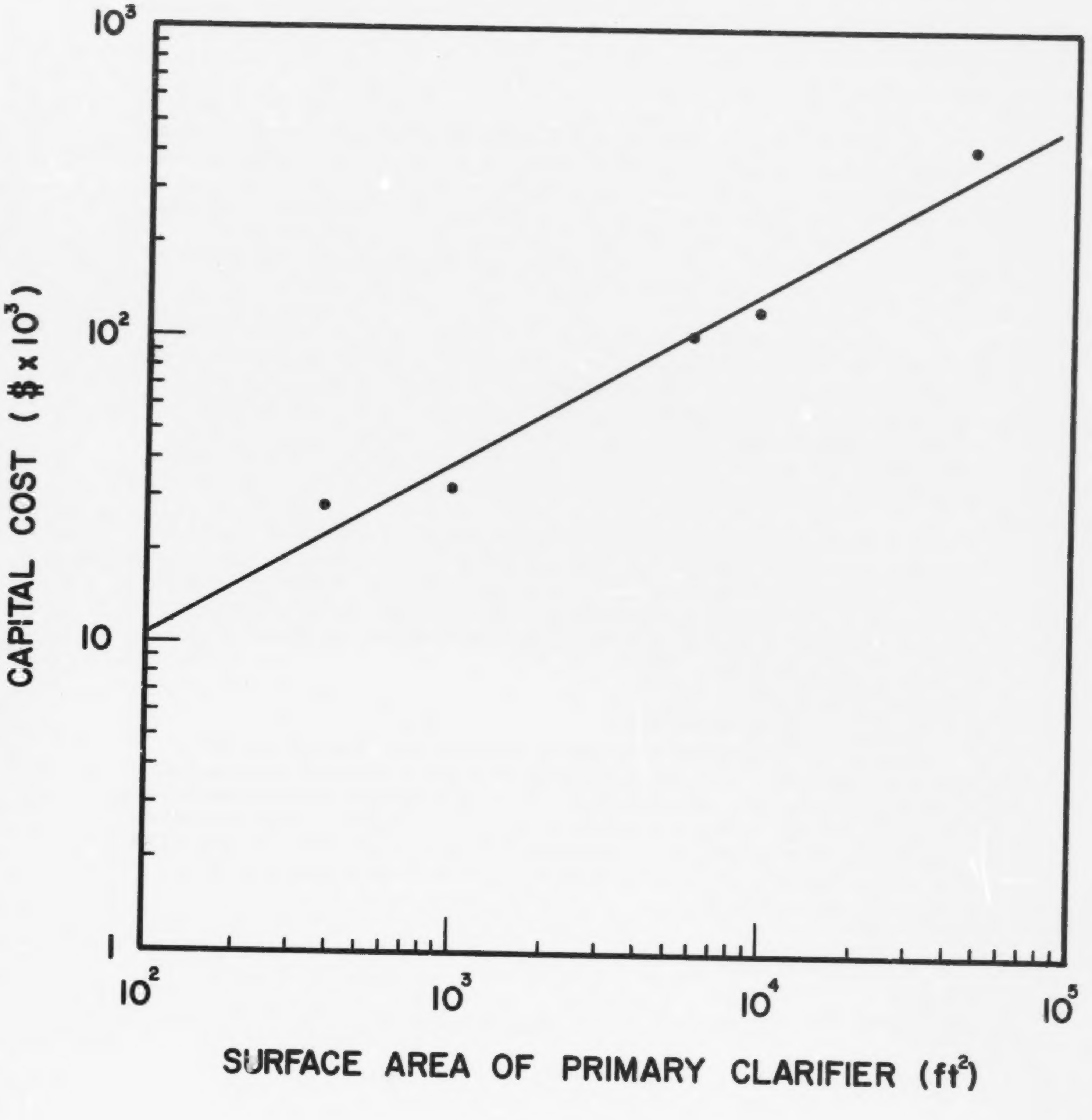


FIGURE VIII-4

CAPITAL COST RELATIONSHIP - PRIMARY SEDIMENTATION

(Reference 4)

The capital cost relationships for waste stabilization ponds, aerated lagoons, and activated sludge basins are shown in Figures VIII-5 through VIII-7. The cost of the waste stabilization ponds is dependent on the land cost, which was not considered in the preparation. Total capital costs of aerated lagoons and activated sludge basins, including aeration equipment, depend on the type of basin construction, subsoil conditions, and aeration system.

The equipment cost of mechanical surface aerators is illustrated in Figure VIII-8. Large aeration units are more economical than small units; however, mixing considerations often necessitate the use of the smaller units and this may take precedence over the economical aspects. Secondary clarifier costs, Figure VIII-9, parallel the costs required for primary clarifiers and are governed by the same considerations.

The unit cost of trickling filters related to waste flow is given in Figure VIII-10. The dispersion of reported values which is observed from this relationship is primarily attributable to differences in the organic loadings applied to the various filters. There are not enough trickling filter units presently treating petrochemical wastes to statistically establish the organic loading effect, but a generalized trend is indicated in Figure VIII-10.

It is difficult to tabulate and compare operating costs of various treatment facilities because of the many different accounting methods, amortization procedures and depreciation schedules used by the industry. However, a tabulation of reported daily operating costs in terms of volume and organic load treated is given in Table VIII-2.

Tertiary Treatment Processes

Tertiary treatment of petrochemical wastewaters is not common. However, cost relationships for the treatment of municipal effluents using ion exchange and carbon adsorption methods have been reported (Smith, 1968; Eckenfelder, et. al., 1968). These correlations have been graphically represented in Figures VIII-11 and VIII-12. This approach considers correcting the flow according to the following expressions.

Ion Exchange -

$$\left[\text{Corrected flow}_{\text{Ind. Waste}}\right] = \left[\text{flow}_{\text{Mun. Waste}}\right]\left[\frac{\text{COD}_{\text{Ind.}}}{\text{COD}_{\text{Mun.}}}\right] \; 0.75$$

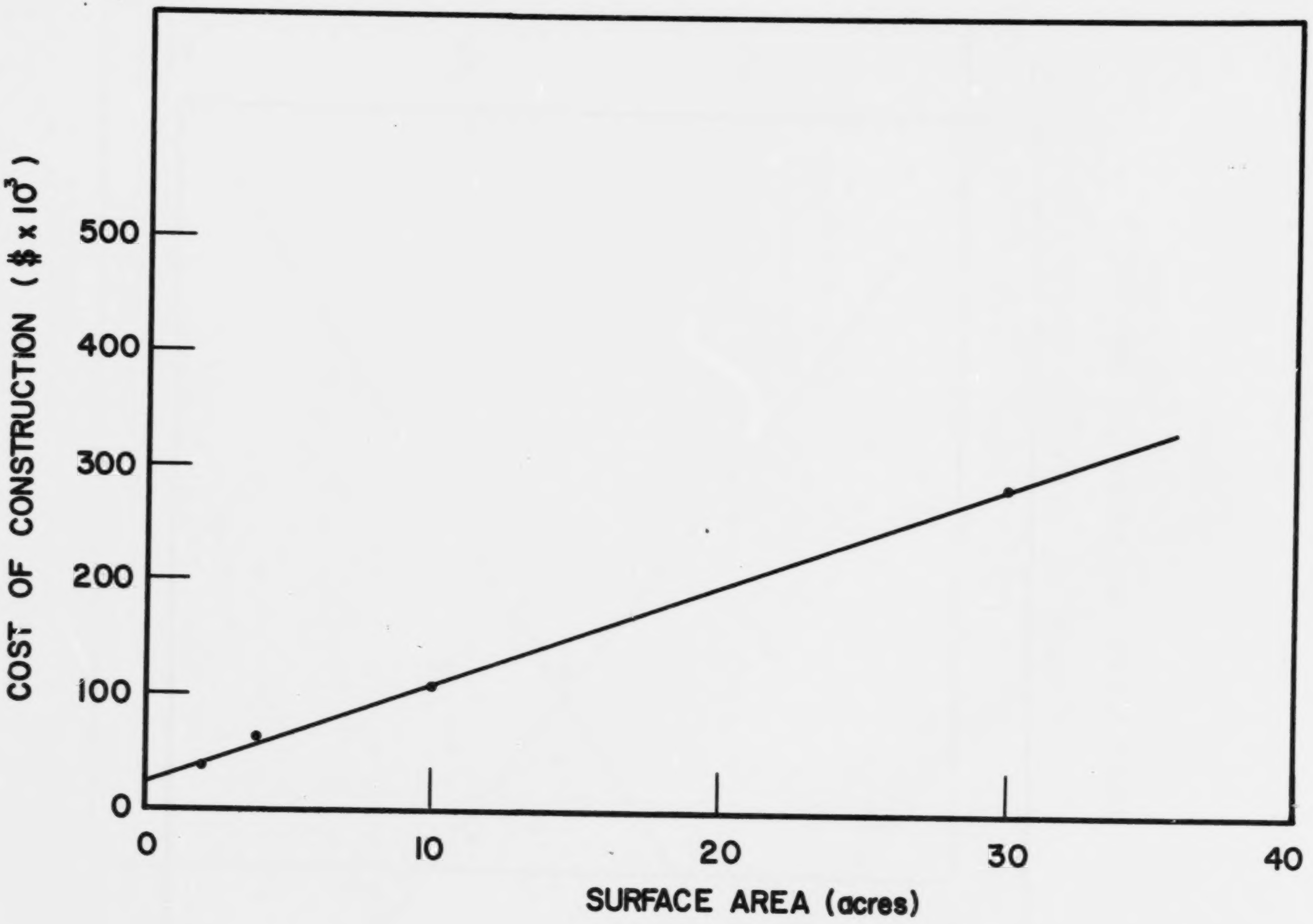


FIGURE VIII-5

CAPITAL COST RELATIONSHIP - LAGOONS

(Reference 4)

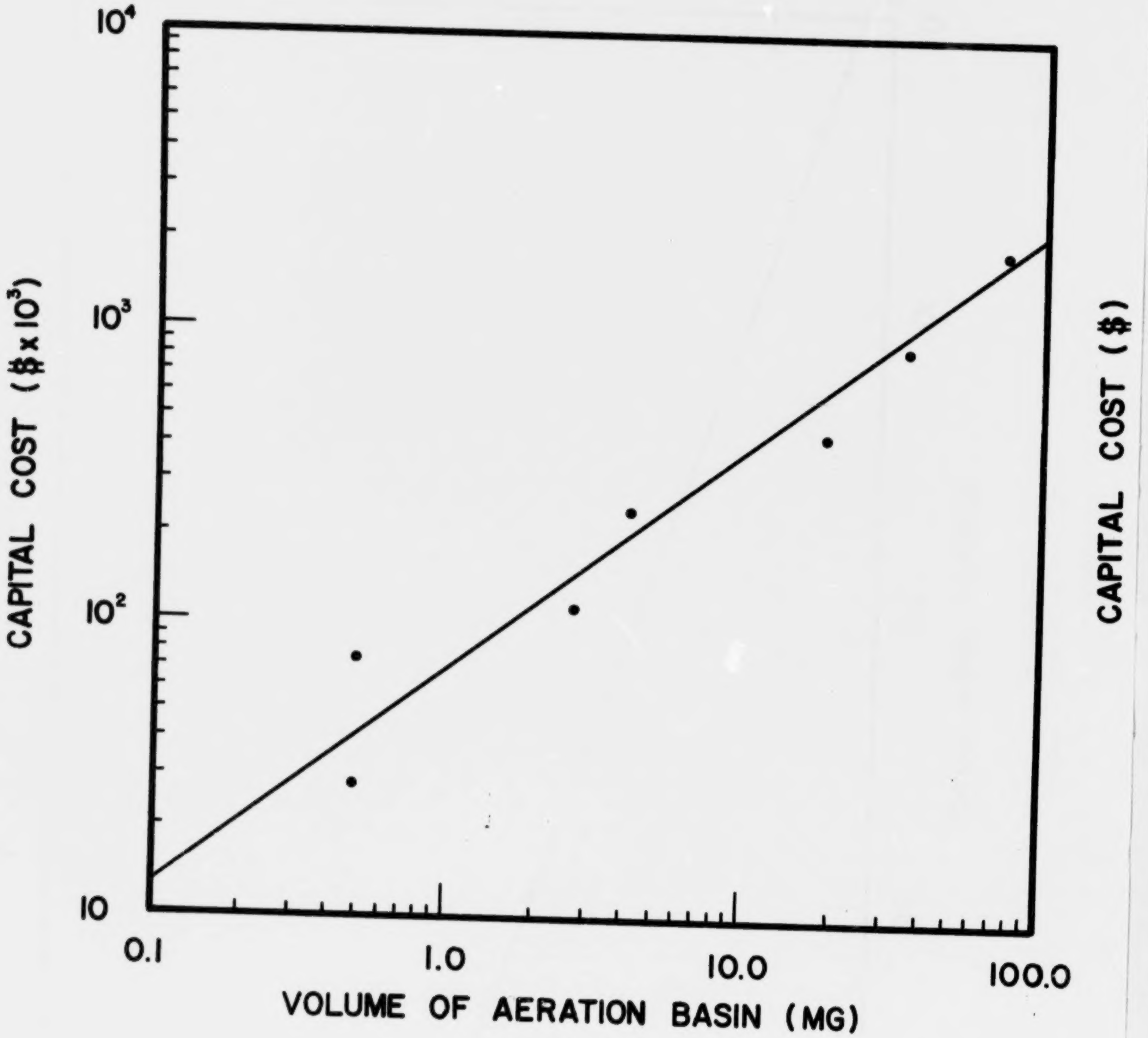


FIGURE VIII-6

CAPITAL COST RELATIONSHIP - AERATED LAGOON
(INCL. AERATION EQUIP.)
(Reference 4)

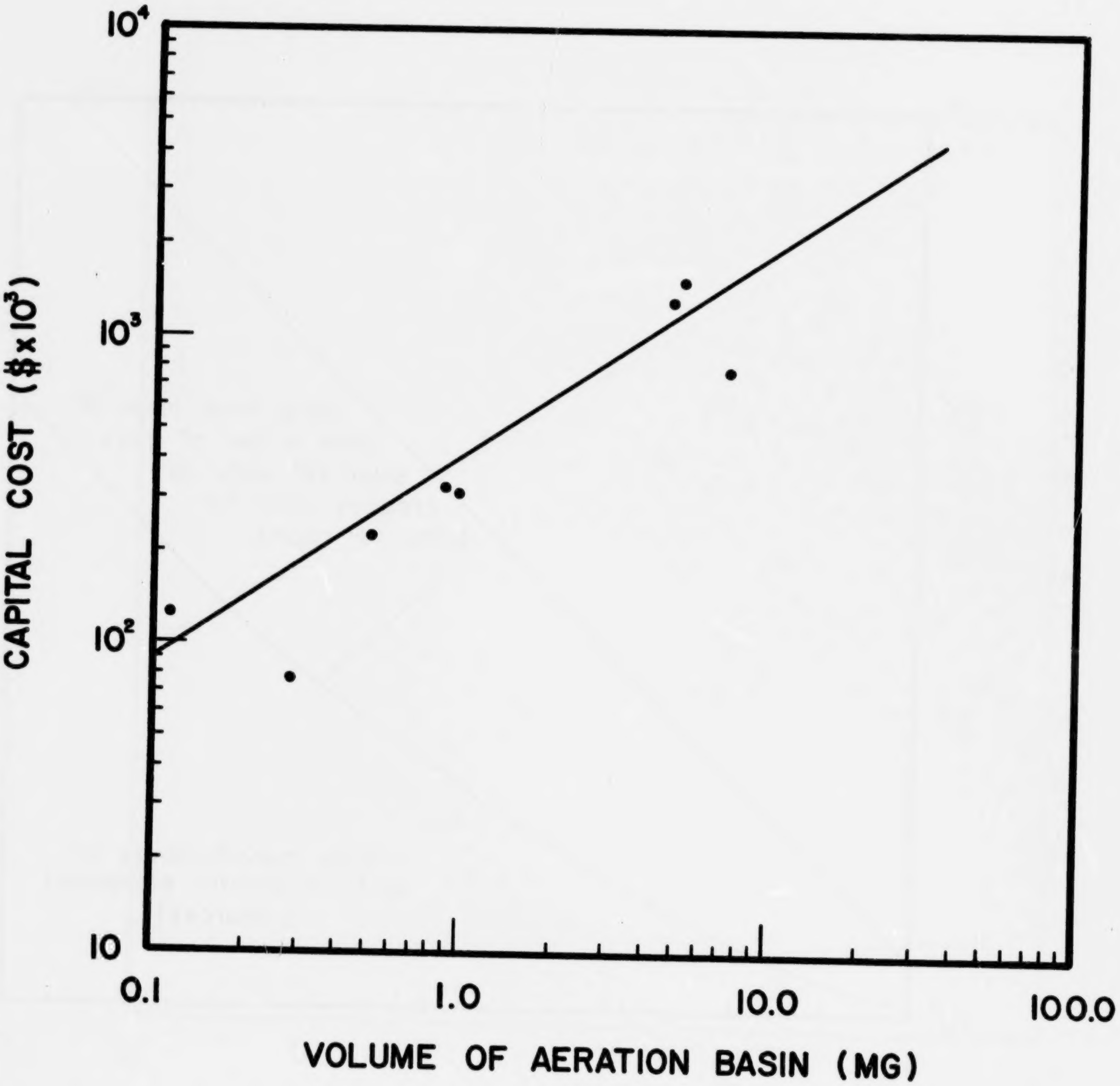


FIGURE VIII-7

CAPITAL COST RELATIONSHIP - ACTIVATED SLUDGE
(INCL. AERATION EQUIP.)

(Reference 4)

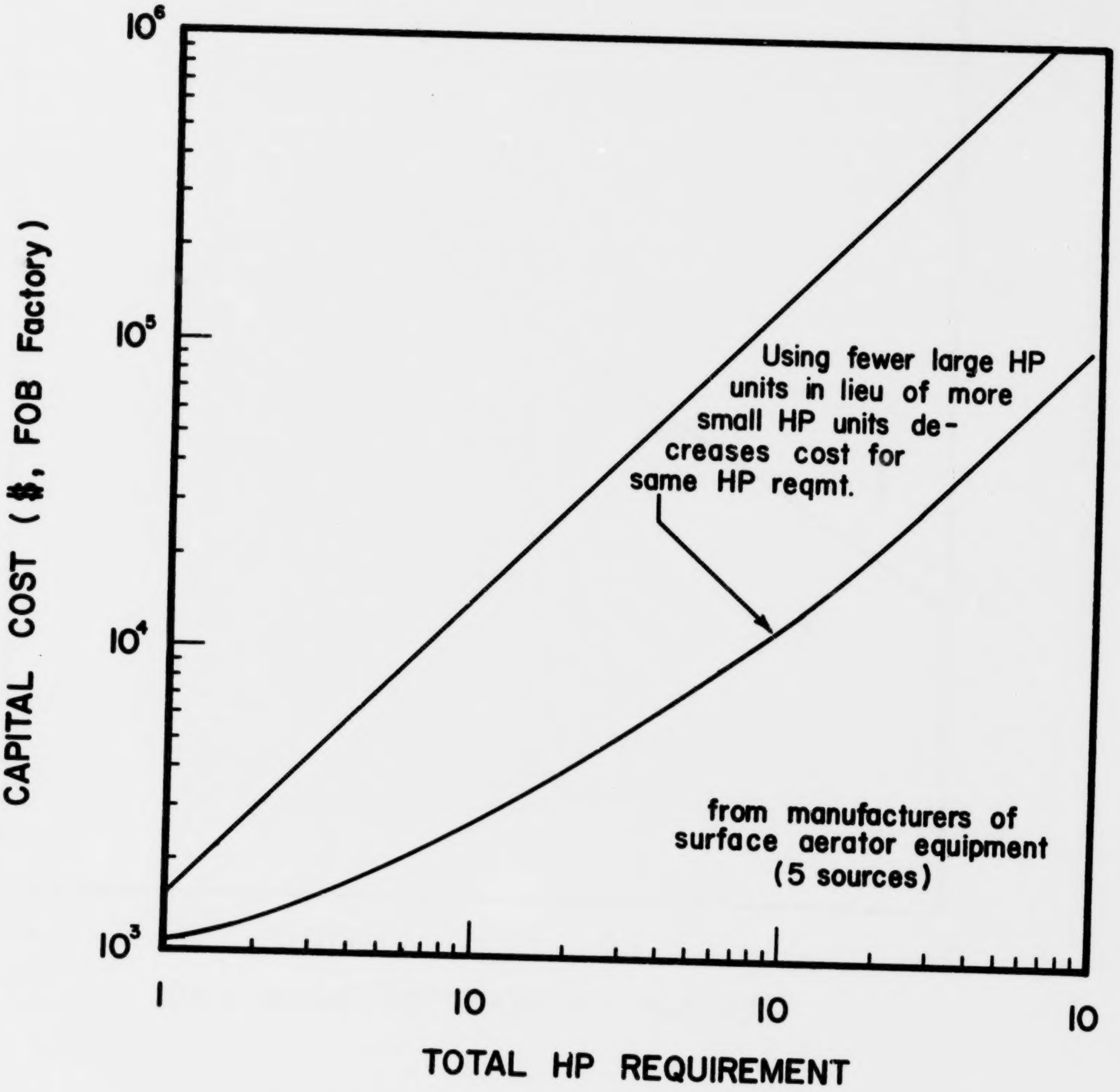


FIGURE VIII-8

MECHANICAL SURFACE AERATORS
(EQUIPMENT COST)

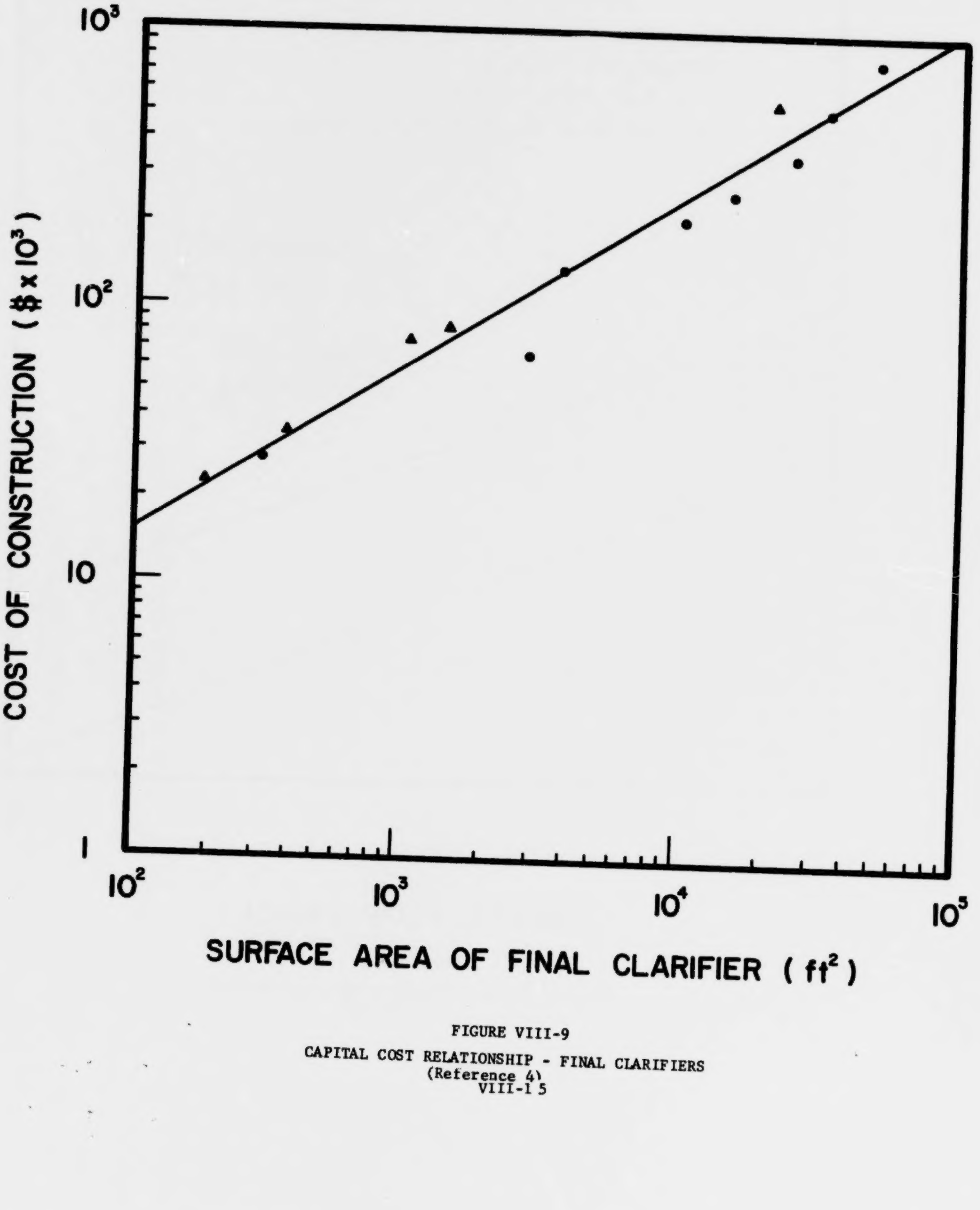


FIGURE VIII-9

CAPITAL COST RELATIONSHIP - FINAL CLARIFIERS
(Reference 4)

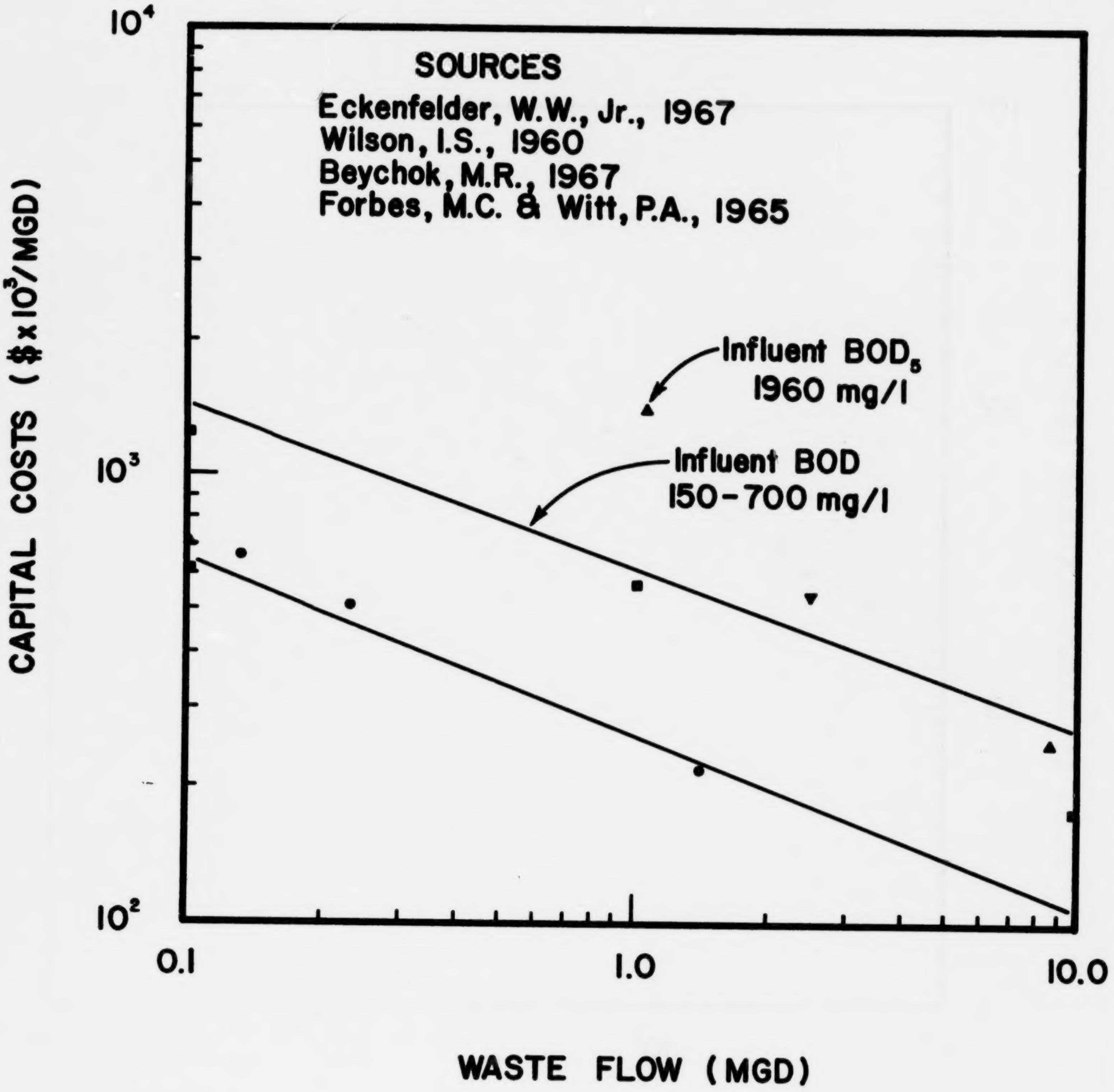


FIGURE VIII-10

CAPITAL COST RELATIONSHIP - TRICKLING FILTERS

TABLE VIII-2

OPERATING COSTS - WASTE TREATMENT PLANTS

(Reference 3)

Industry	Type of Treatment	Daily Operating Costs		No. Plants Reporting	Solids Disposal
		$/MG	$/1,000 lb Pollutant		
Refinery	Primary-includes oil separation, coagulation, flotation, and sedimentation	126-160	26-150 (COD)	4	Vacuum Filter Landfill Incineration
	Secondary-				
	Activated Sludge	161	292 (COD)	1	Landfill
	Aerated Lagoon	22	9 (COD)	1	-
	Extended Aeration	28	14 (COD)	1	Holding Ponds
Chemical	Primary-all types including oil separation, coagulation, flotation sedimentation, neutralization, and equalization	11-1,540	3-40 (S.S.)	11	Landfill Incineration Vacuum Filter Lagoons
	Secondary				
	Aerated Lagoon	31-1,160	6-477 (BOD)	4	Landfill

TABLE VIII-2 (Continued)

OPERATING COSTS - WASTE TREATMENT PLANTS

Industry	Type of Treatment	Daily Operating Costs		No. Plants Reporting	Solids Disposal
		$/MG	$/1,000 lb Pollutant		
Chemical (Cont.)					
	Secondary (Cont.)				
	Activated Sludge				
	Conventional	1,580	100 (BOD)	1	-
	Extended Aeration	221-276	7-734 (BOD)	5	Landfill, Lagoon
	Contact Stabilization	16-211	23-106 (BOD)	2	Landfill
	Trickling Filter	780-2,050	49-3,750 (BOD)	2	Lagooning
	Facultative Pond	163	39 (BOD)	1	Burning
	Combination				
	Trickling filter and activated sludge	334-378	28-245 (BOD)	2	Landfill

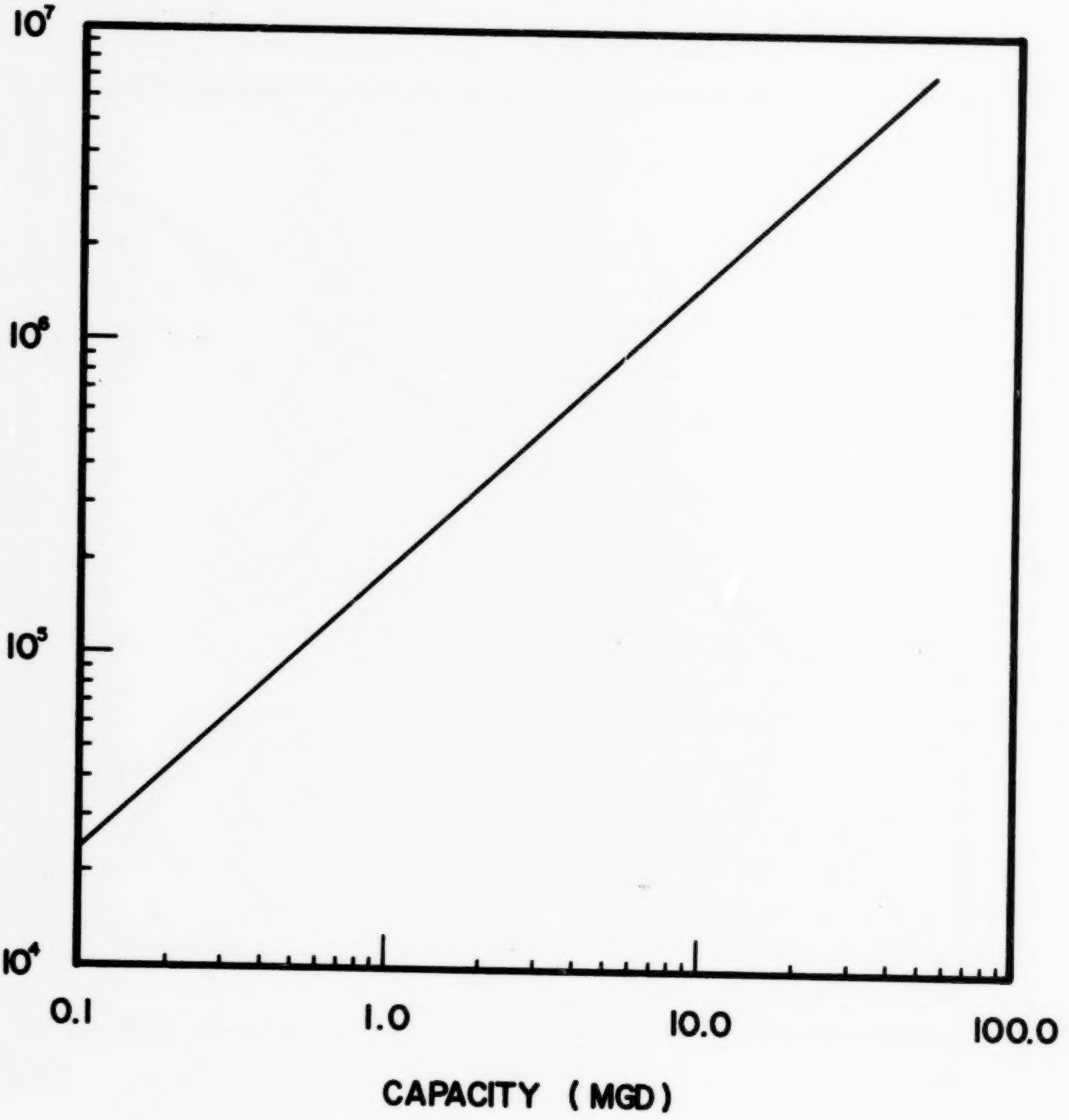


FIGURE VIII-11

CAPITAL COST RELATIONSHIP - ION EXCHANGE

(Reference 9)

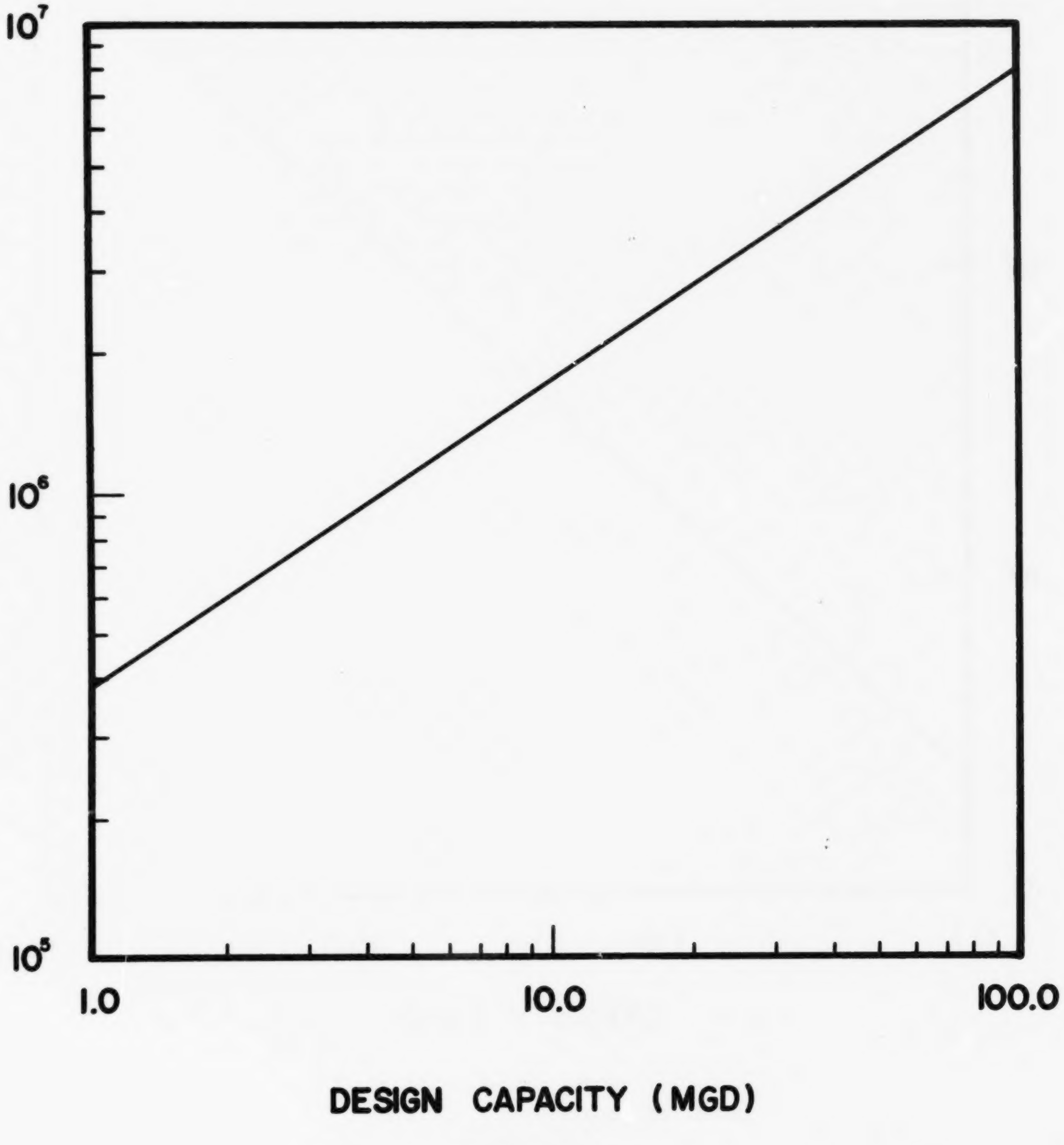


FIGURE VIII-12
CAPITAL COST RELATIONSHIP - CARBON ADSORPTION
(Reference 9)

Carbon Adsorption -

$$\left[\text{Corrected flow}_{\text{Ind. Waste}}\right] = \left[\text{flow}_{\text{Mun. Waste}}\right]\left[\frac{\text{Total Dissol. Solids}_{\text{Ind.}}}{350}\right] 0.75$$

The corresponding capital costs for the corrected flows can then be determined.

Sludge Handling and Disposal Processes

Capital cost relationships for sludge handling using flotation thickening and vacuum filtration are developed in Figures VIII-13 and VIII-14. The flotation thickening correlaton is based on data made available primarily from the petroleum refining industry (Beychok, 1967), while the vacuum filter description is predicated on municipal waste treatment experience (Smith, 1968).

A total sludge disposal-cost relationship based on questionnaire information reported by chemical and petrochemical industries is shown in Figure VIII-15. The costs indicated for a given waste flow include aerobic digestion, sludge thickening, vacuum filtration or centrifugation, and disposal. The obvious significance of wastewater suspended solids concentration and the nature of the resultant sludge is not considered here, but again, a generalized estimate based solely on wastewater flow can be formulated.

Ultimate Disposal

The petroleum refineries reporting to a 1965 survey indicated that the total replacement cost for their waste treatment facilities would be $156,000,000 (Anon., Water in Ind., 1965). This report also indicated that 134 refineries are planning future treatment facilities and process modifications which will cost $129,500,000. A similar report from the chemical industry showed a present investment of $263,600,000 in waste treatment plants, with facilities costing approximately $70,000,000 planned for the next five years (Anon., Water in Ind., 1965). The cost of incinerating liquid wastes and slurries is shown in Figure VIII-16. Operating and capital costs, based on a 20-year amortization schedule, are included.

The annual operating budget for a waste treatment facility which includes two disposal wells, a trickling filter, an activated sludge plant and an incinerator, including amortization is $750,000 (Sadow, 1966).

RETURNS TO THE PETROCHEMICAL INDUSTRY

The petrochemical industry can appreciate a direct economic return through water reuse. Generally, industry pays from $.02 to $.35 per 1,000 gallons for treated water while recycled cooling water can be purchased for as little as $.01 to $.05 per 1,000 gallons (Clarke, 1962). Therefore, it can be stated that

a) certain costs are associated with obtaining a supply of water, conditioning or treating it for use, and properly disposing of the waste;

b) certain costs are associated with the alternative of treating wastewater for direct reuse, thus minimizing the purchase and disposal costs; and

c) when the costs of (b) are less than those of (a), an economic return in the form of water reuse can be appreciated.

The second mechanism of realizing an economic return to the industry is in the form of product recovery. This determination must be predicated on the recovery cost-market value economics, recognizing that a reduction in waste treatment costs is normally associated with product recovery.

All of the aforementioned factors merit an engineering and economic review, the implementation of which may produce a monetary return to the industry.

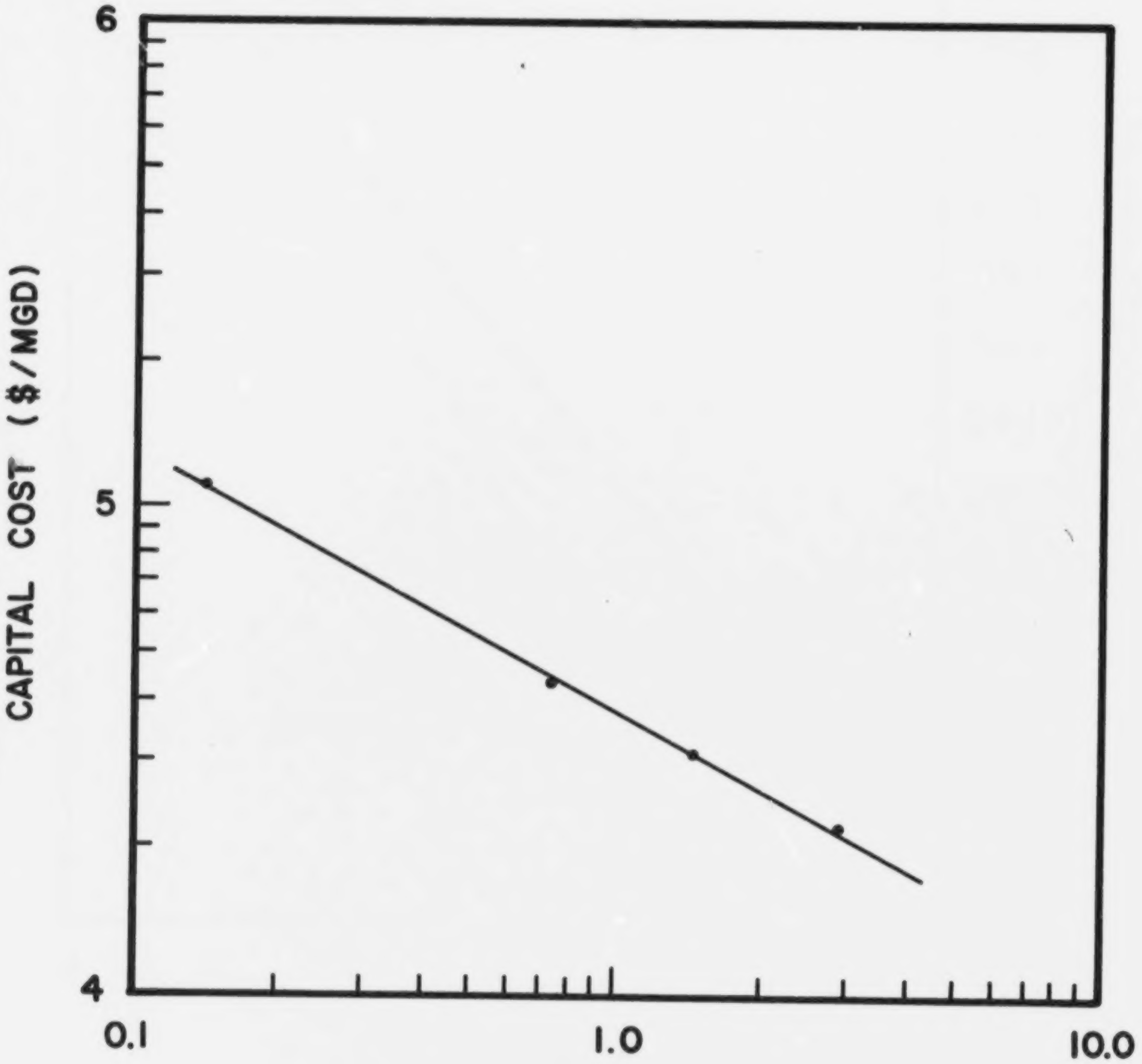


FIGURE VIII-13

CAPITAL COST RELATIONSHIP - FLOTATION THICKENING

(Reference 2)

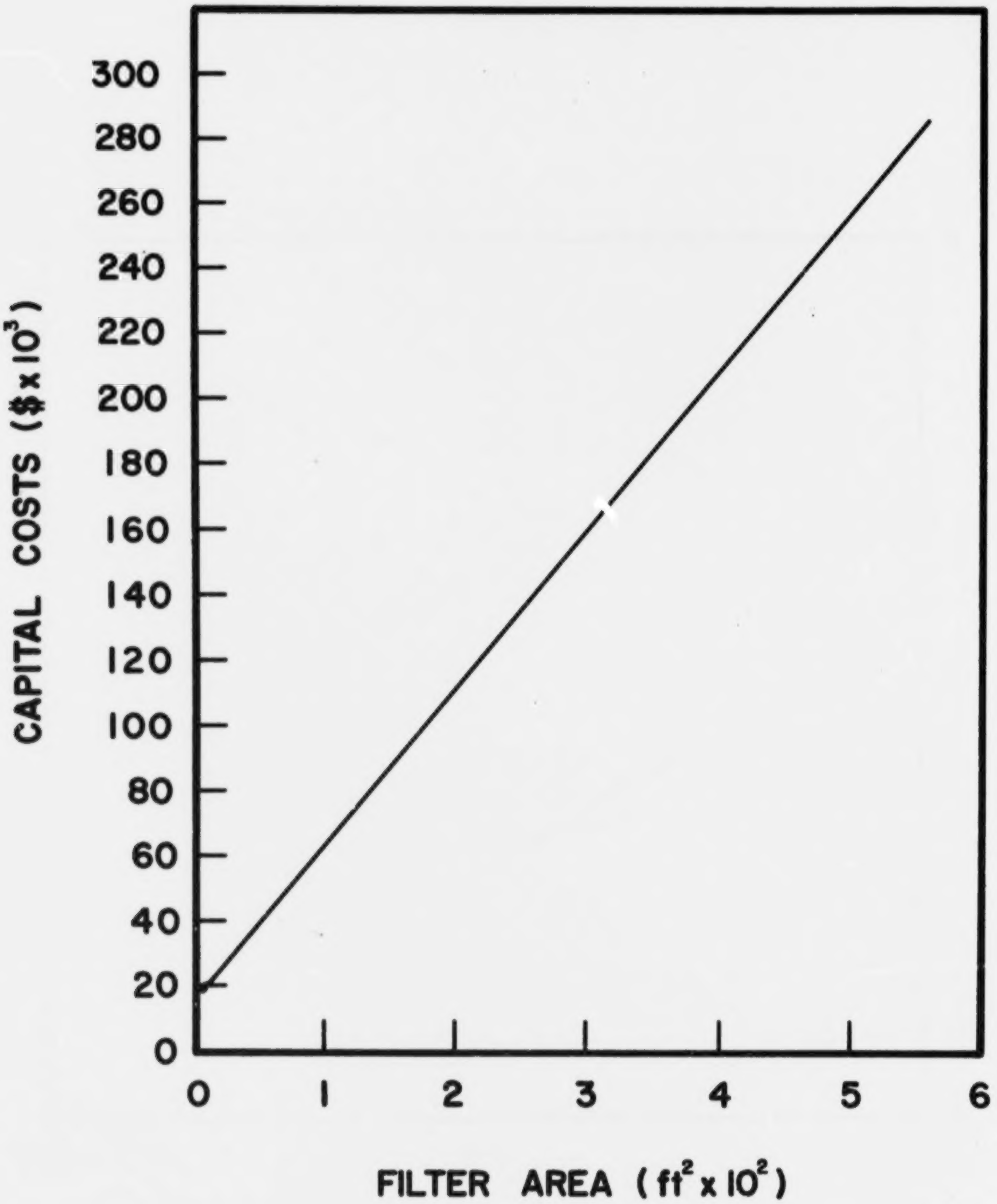


FIGURE VIII-14

CAPITAL COST RELATIONSHIP - VACUUM FILTRATION

(Reference 9)

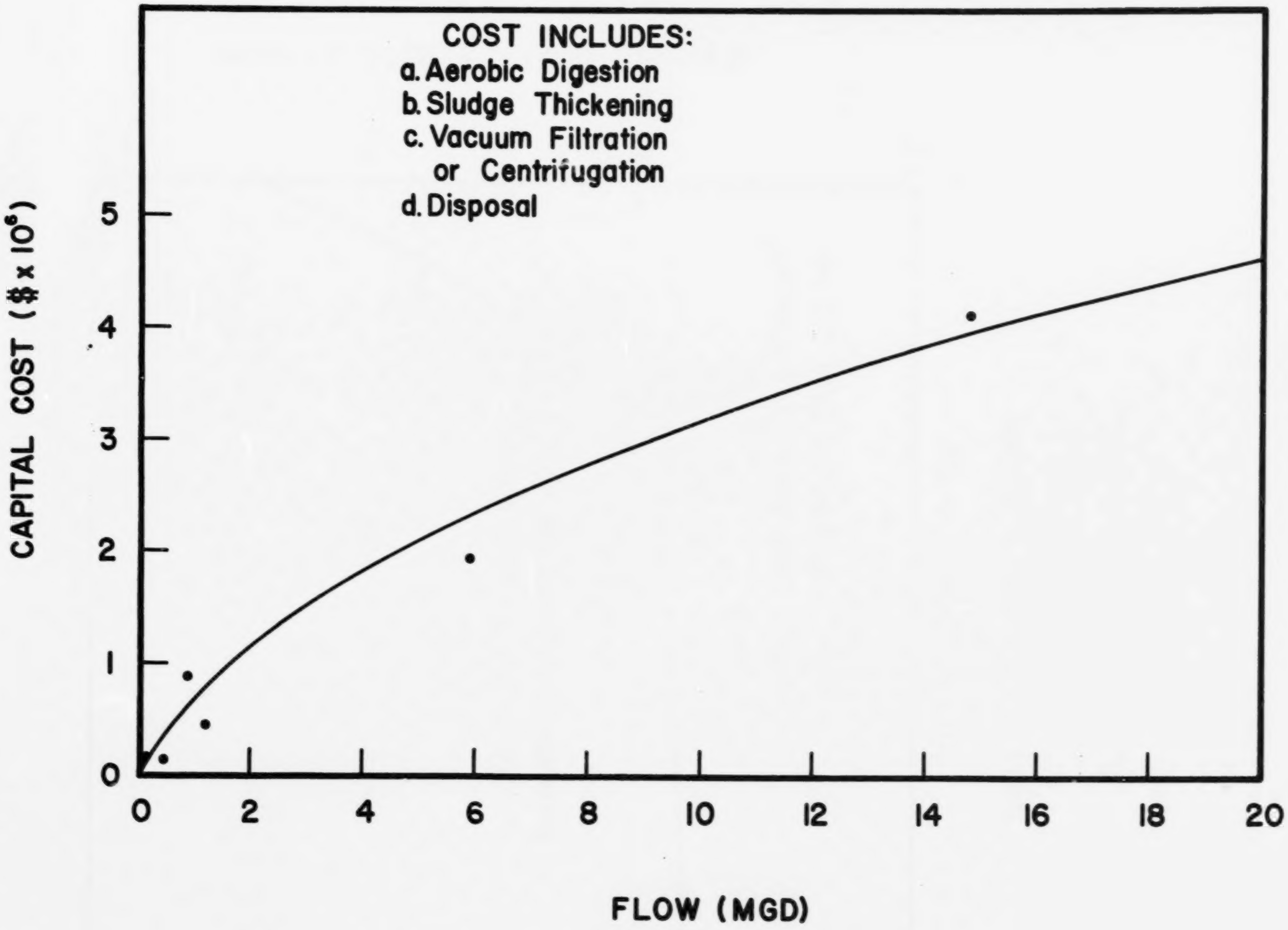


FIGURE VIII-15

CAPITAL COST RELATIONSHIP - TOTAL SLUDGE DISPOSAL

(Reference 4)

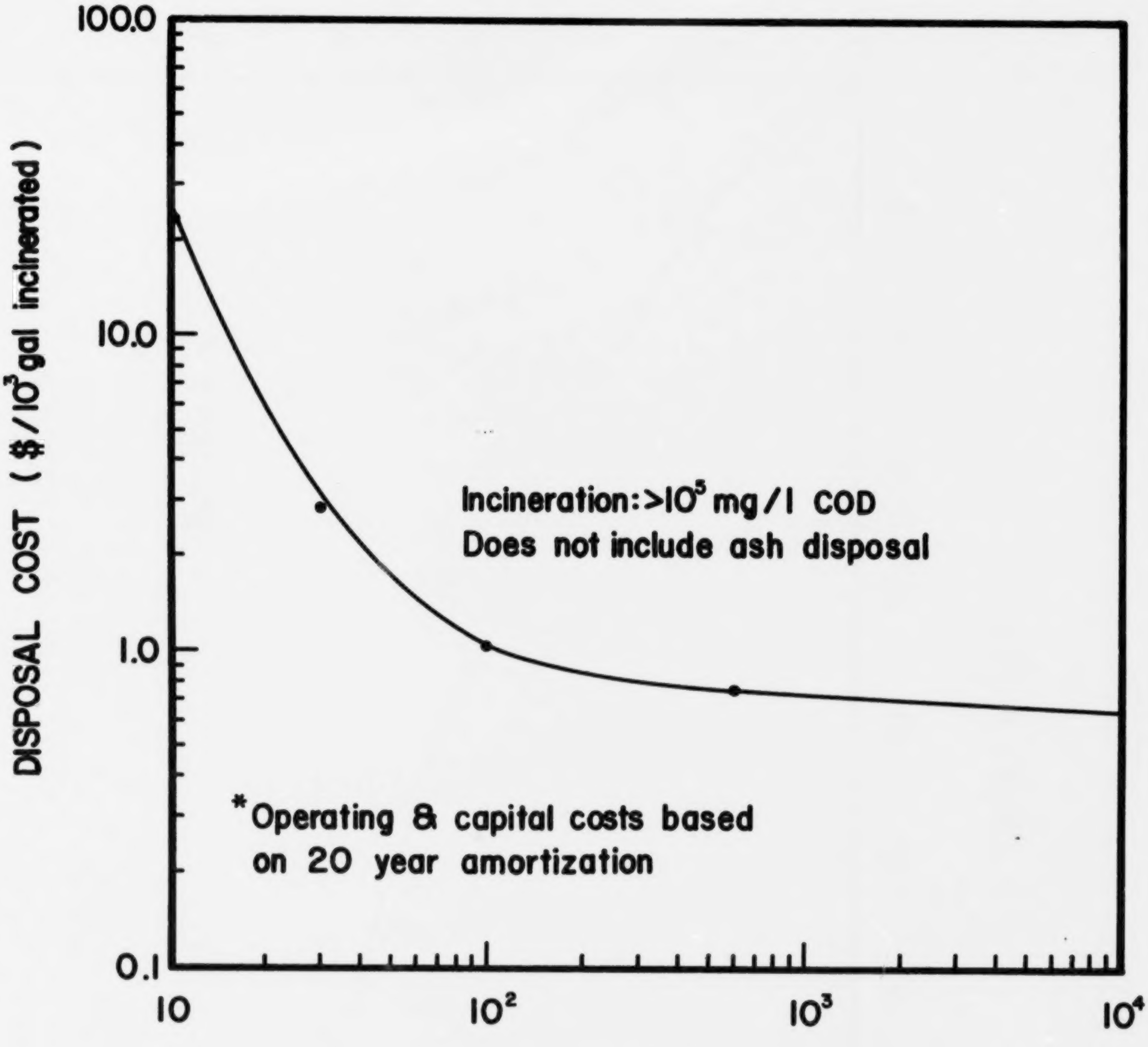


FIGURE VIII-16

CAPITAL COST RELATIONSHIP* - INCINERATION
(Reference 6)

REFERENCES - CHAPTER VIII

1. Anon., *Water in Industry*, National Assoc. of Manufacturers and the Chamber of Commerce of the U. S., New York and Washington, D. C. (1965).

2. Beychok, M. R., *Aqueous Wastes from Petroleum and Petrochemical Plants*, John Wiley & Sons, London (1967).

3. Eckenfelder, W. W., Jr., "Effluent Quality and Treatment Economics for Industrial Wastewater," Rept. to FWPCA, Washington, D. C. (1967).

4. Eckenfelder, W. W., Jr., *et. al*., Unpublished Rept. (1968).

5. Forbes, M. C. and Witt, P. A., "Estimate Cost of Waste Disposal," *Hydrocarbon Processing*, v. 44, n. 8, p. 153 (1965).

6. Koenig, L., "Ultimate Disposal of Advanced Treatment Waste," USPHS, Publ. No. 999-WP-3, Cincinnati, Ohio (1963).

7. Rice, C. W. and Company, Eckenfelder, W. W., Jr. and Associates and Weston, R. F., Inc., *Projected Wastewater Treatment Costs in the Organic Chemicals Industry*, Unpublished Rept. to the FWPCA (January 1969).

8. Sadow, R. D., "Waste Treatment at a Large Petrochemical Plant," *J. WPCF*, v. 38, n. 3, p. 428 (March 1966).

9. Smith, R., "Cost of Conventional and Advanced Treatment of Wastewater, *J. WPCF*, v. 40, n. 0, p. 1546 (Sept. 1968).

10. Wilson, I. S., "The Treatment of Chemical Wastes," *Waste Treatment*, Isaac, P. C. G., ed., Pergamon Press, London, p. 206 (1960).

APPENDIX I

Process Information

A - Primary Petrochemicals

B - Common Intermediate Petrochemicals

C - Third-Generation Petrochemicals

I-A PROCESSES FOR PRIMARY PETROCHEMICALS

PRODUCT	FEEDSTOCK	REACTION SEQUENCE	TEMP. (° C)	PRESSURE (psig)	CATALYSTS	REMARKS
Acetylene	1. light paraffins, steam	v.p. thermal cracking v.p. purification	~1,133	-7.3	-	Heat supplied by fuel gas ethylene co-prod. C_3HC by-products.
	2. Natural gas, O_2	v.p. partial oxidation v.p. purification	-			
Aromatics (Benzene Toluene, Xylene	1. Aromatic fraction from reformer	l.p. solvent extraction v.p. stripping l.p. fractionation	- - -	- - -	-	Note: direct recovery
Benzene	1. See Aromatics	direct recovery				
	2. Toluene/Xylene, H_2	l.p. hydrodealkylation (thermal) or hydrodealkylation (catalytic)	594-760	500-1,000	-	CH_4 by-product CH_4 by-product
Butenes	1. Refinery streams	direct recovery				
	2. Butanes	v.p. dehydrogenation			Cr oxide on alumina	Butane feed determine butene formed
Cyclohexane	1. Natural gas liq.	direct recovery	-	-	-	Small amounts
	2. Benzene, H_2	l.p. hydrogenation	-	-	precious metals	Major source
Ethylene and Propylene	1. Various refinery streams	direct recovery	-	-	-	-
	2. Refinery gas, ethane, propane, butane, nat. gas, light refinery fractions, heavy distillates	v.p. pyrolysis (thermal)	750-900	-	-	Ethylene, propylene, butene formed by-products: acetylene, methane, aromatics
Hydrogen	1. Refinery off-gases	direct recovery	-	-	-	-
	2. Synthesis gas	v.p. water gas conversion of CO & steam (catalytic)	-	-	-	CO_2 by-product
	3. Any hydrocarbon	decomposition (catalytic)				Carbon by-product

I-A PROCESSES FOR PRIMARY PETROCHEMICALS (Continued)

PRODUCT	FEEDSTOCK	REACTION SEQUENCE	TEMP. (^{o} C)	PRESSURE (psig)	CATALYSTS	REMARKS
Synthesis Gas	1. Naphthas/refinery gas/H.C., steam, air	v.p. reforming (catalytic)	700-850	350-550	Ni	CH_4, CO_2, by-product (two stages)
	2. Hydrocarbons, air or O_2	v.p. partial oxidation	-	-	None	Thermal; CH_4, CO_2 by-product
Naphthalene	2. Alkynaphthalenes	hydrodealkylation (catalytic)	-	-	-	CH_4 by-product

l.p. liquid phase

v.p. vapor phase

(-) indicates data not available

I-B PRODUCTION OF COMMON INTERMEDIATE PETROCHEMICALS

PRODUCT	FEEDSTOCK	REACTION SEQUENCE	TEMP. (° C)	PRESSURE (psig)	CATALYSTS	REMARKS
Acetaldehyde	1. Ethanol	v.p. dehydrogenation	275-280	-	Cu & Co; Cr on abestos	-
	2. Ethanol, air	v.p. oxidation, dehydrogenation	550	-	Ag	-
	3. Butane/Propane, oxygen	v.p. oxidation	430-530	100-300	Noncatalytic	Formaldehyde, methanol, acetone by-products
	4. Ethylene, oxygen or air	l.p. oxidation	20-100	120	$CuCl_2$, $PdCl_2$	Polladium chloride sol. is oxygen carrier
	5. Acetylene, water	l.p. hydration	80-95	-	HgO	Minor process in U.S.
Acetic Acid	1. Acetaldehyde, air or oxygen	l.p. oxidation	50-70	-	$MnC_2H_3O_2$	Exothermic
	2. Acetaldehyde, oxygen, olefins	l.p. or v.p. oxidation to acetaldehyde peracetate	-5-0	-	-	
	3. Butane, air or hexane, air	l.p. oxidation or l.p. oxidation	165-170 170	815 1,170	$CrC_2H_3O_2$ Noncatalytic	Acetic acid solvent By-products: formic & propionic acids, esters ketones
	4. Methanol, carbon monoxide	l.p. reaction	250	9,580	Cobaltous Iodide	Propionic acid by-product
Acetic Anhydride	1. Acetaldehyde, air or oxygen	l.p. oxidation	-	-	Cobalt acetate-copper acetate	-
	2. Acetic acid	v.p. cracking to ketone	740	-	Triethyl phosphate	
		l.p. reaction of ketene & autic acid	-	-	-	Fractionation req'd tc separate anhydride from acid.
	3. Acetone, acetic acid	v.p. cracking of acetone to ketene quench ketene with acetic acid to produce anhydride	750-800	(-12.5)-(-11.6)	-	CS_2 added to suppress carbon formation

I-B PRODUCTION OF COMMON INTERMEDIATE PETROCHEMICALS (Continued)

PRODUCT	FEEDSTOCK	REACTION SEQUENCE	TEMP. (° C)	PRESSURE (psig)	CATALYSTS	REMARKS
Acetone	1. Isopropanol	l.p. dehydrogenation	150	-	Ni	-
		v.p. dehydrogenation	380	0	Zn O	Diisopropylethen and propylene by-products
	2. Propylene, air	l.p. oxidation	100	-	Pd Cl_2, Cu Cl_3	-
	3. Cumene, air	l.p. autooxidation	110-130	-	copper porphyrins	pH 8.5-10
		l.p. clearage	45-65	-	sulfuric acid	Phenol is co-product
	4. Acrolein	v.p. reduction	350-450	-	Mg O - Zn O	Allyl alcohol is primary product, acetone is co-product
	5. Isopropanol, oxygen	l.p. oxidation	90-140	200-300	H_2O (autocatalytic)	Hydrogen peroxide co-product
Acrolein	1. Propylene, air	v.p. oxidation	400	-	Cu O or Bismuth phosphomolybdate	-
Acrylates	1. Acetylene, carbon monoxide, alcohols	l.p. formylation of acetylene	225	1,455	Ni (CO_4), HCl	Tetrahydrofuran Solvent
		l.p. esterification with alcohol	45-50	0		Acetaldehyde by-product
	2. Ketene, formaldehyde, alcohol	v.p. formylation of ketene alcohol quench	250-260	-	BF_3	diluted with N_2 prior to quench
	3. Ethylene oxide hydrogen, cyanide, alcohol	l.p. condensation to ethylene cyanohydrian	55-60	-	NaOH, diethylamine	
		l.p. reaction with alcohol	150	-	Sulfuric acid or ion exchange resin	
Acrylonitrile	1. Acetylene, HCN	l.p. condensation	80-90	15	Cu Cl_2	
	2. Propylene, ammonia, air	v.p. oxidation to acrolein	400	-	CuO or Bismuth phosphomolybdate	
		v.p. conversion to acrylonitrile	380	-	MoO_3 on alumina Uranium based	
		or				

I-B PRODUCTION OF COMMON INTERMEDIATE PETROCHEMICALS

PRODUCT	FEEDSTOCK	REACTION SEQUENCE	TEMP. (° C)	PRESSURE (psig)	CATALYSTS	REMARKS
Acrylonitrile (Cont.)		v.p. ammoxidation	380-510	5-30	Bismuth phosphomolybdate or Bismuth vanadotungstate	Acetonitrile & HCN by-products fluid or fixed bed process
	3. Propylene, NO	v.p. reaction	460-500	-	Ca promoted Ag	
	4. Ethylene oxide, HCN	l.p. condensation to ethylene cyanhydride	55- 60	-	NaOH, diethylamine	
		l.p. dehydration	200	-	Mg CO_3	
	5. Acetaldehyde, HCN	l.p. Lactonitrile formation	10- 20	-	None	
		v.p. dehydrogenation	600-700	-	H_3PO_4	
Adipic Acid	1. Cyclohexanol, cyclohexanone, HNO_3	l.p. oxidation	60- 80	-	Cu, V	
	2. Cyclohexanol, cyclohexanone, air	l.p. oxidation	180- 85	-	Mn & Cu acetates	Acetic acid solvent
Adiponitrile	1. Butadiene, HCN, Cl_2, H_2	v.p. chlorination (also l.p.)	65- 75	-		
		l.p. reaction with HCN	95	-	CuCl HCI	
		l.p. hydrogenation	250-300	-	Pd	Alternate routes
		OR				
		v.p. hydrogenation	75-150		Pd	
	2. Adipic acid, NH_3	v.p. condensation - dehydration	360		Boron phosphate or silico phosphoric acid	
	3. Acrylonitrile	electrolytic reduction				Not yet commercial

I-B. PRODUCTION OF COMMON INTERMEDIATE PETROCHEMICALS (Cont.)

PRODUCT	FEEDSTOCK	REACTION SEQUENCE	TEMP. (° C)	PRESSURE (psig)	CATALYSTS	REMARKS
Aldehydes	1. Olefins, CO, H_2	l.p. hydrocarboxylation (OXO)	140-175	1,500-4,000	Cobalt hydrocarboxylation	
Alcohols, long chain primary	1. Ethylene, triethyl aluminum, H_2SO_4, air	l.p. buildup reaction	160	2,185	Cu	
		l.p. oxidation	95	0		
		l.p. fission (w/H_2SO_4)	40	0		
Alpha Olefins, linear	1. Ethylene, triethyl aluminum	l.p. buildup reaction	160	2,185	Cu	
		l.p. displacement	285	1,455	None	
	2. Linear paraffins	v.p. cracking	550-575	-	-	Mixed olefins in products stream
Aniline	1. Nitrobenzene, H_2	v.p. hydrogenation	200-350	> 0	$CuCO_3$ or Nickel sulfide	
		v.p. hydrogenation	270	20	Cu or silicon	
	2. Chlorobenzene, NH_3	l.p. ammonolysis	200-210	850-950	CuO	Phenol & diphenylamine by-products
	3. Nitrobenzene, iron filings	hydrogenation	-	-	iron filings	Used only is small plants
Bisphenol-A	1. Phenol, acetone	l.p. condensation	50- 70	-	HCl or HBr promoted by methylmercaptan	
1,3 Butadiene	1. n-Butene	v.p. dehydrogenation	620-675	~ 0	Fe_2O_3+Cr_2O_3 + K_2CO_3	Alternates
			500-675	~ 0	Mg-Fe oxide	
			595-675	~ 0	Ca-Ni phosphate	
			650	~ 0	Chromia-alumina	
	2. n-Butane	v.p. dehydrogenation	600-650	-11.7	Chromia-alumina	

I-B PRODUCTION OF COMMON INTERMEDIATE PETROCHEMICALS (Continued)

PRODUCT	FEEDSTOCK	REACTION SEQUENCE	TEMP. (° C)	PRESSURE (psig)	CATALYSTS	REMARKS
Butanol	1. Acetaldehyde	l.p. aldol condensation	5-25	~ 0	Caustic	
		l.p. dehydration	95		Sodium acid Phosphate	
		v.p. hydrogenation	200		Cu or Ni	n-Butanol,
	2. Propylene, CO, H_2O	l.p. reaction	100	2,200	Iron pentacarbonyl butylpyrrolidine	n-Butanol, i-butanol
	3. n-Buteneori-butene, H_2SO_4, H_2O	l.p. sulfation	60-70	225-350		Sec-butanol, tert-butanol
		l.p. hydrolysis	b.p.	~ 0		
	4. n-butene, orebutene, H_2O	v.p. hydration	300	1,000	H_3PO_4 or tungsten oxide	Sec-butanol tert-butanol
Butyric Acid	1. n-Butyraldehyde air or oxygen	l.p. oxidation	50-70	-	Mn acetate	Exothermic
n-Butyraldehyde	1. See aldehydes					
Caprolactam	1. Cyclohexanone, hydroxylamine sulfate, H_2SO_4, NH_3	l.p. formation of cyclohexanone oxime	20	-	-	
		l.p. Beckmann rearrangement	140			
	2. Cyclohexane, HNO_3, H_2, H_2SO_4, NH_3	l.p. nitration	80-85	-	-	
		l.p. reduction to cyclohexanone oxime	140	500	Pd, Pb oxide or carbonate	
		l.p. Beckman rearrangement				
	3. Toluene, air, H_2, NH_3, oleum	v.p. oxidation to benzoic acid	160	132		1st reaction can be skipped if benzoic acid is used
		l.p. hydrogenation	170	132	Pd	
		l.p. reaction with nitrosylsufuric acid	55-65	-	H_2SO_4	$(NH_4)_2SO_4$ by-product

I-B PRODUCTION OF COMMON INTERMEDIATE PETROCHEMICALS (Continued)

PRODUCT	FEEDSTOCK	REACTION SEQUENCE	TEMP. ($^{\circ}$ C)	PRESSURE (psig)	CATALYSTS	REMARKS
Caprolactam (Continued)	4. Benzene, H_2, NH_3, oleum, SO_2	v.p. hydrogenation to cyclohexane				
		v.p. oxidation to cyclohexane	150-160	112-117	Co	$(NH_4)_2SO_4$ by-product
		See process #1 above				
	5. Cyclohexane, NH_3, NaCl, H_2SO_4	l.p. photochemical reaction to cyclohexanone oxime HCl	15			
		l.p. Beckmann rearrangement	140			$(NH_4)_2SO_4$ by-product
Carbon Disulfide	1. Methane, sulfur	v.p. catalytic conversion or	600	15-25	Various incl. Si, Al, Mg, Zr, Ni, Co oxides	
		v.p. catalytic conversion	680-700	15-25	Activated bauxite	
Carbon Tetrachloride	1. Methane, chlorine	v.p. chlorination (2 steps)	370-520	-	None	By-products HCl, chlorinated methanes
	2. Carbon disulfide, chlorine	v.p. chlorination (2 steps)	30 60	- -	Iron oxide	Step 1 Step 2 CCl_4 only
	3. Methane, HCl, O_2	v.p. hydrochlorination	-	-	Copper chloride	Mixed chlorinated methanes
Chlorinated Methanes (Chloroform, etc)	See Processes 1 & 3 for CCl_4					
Chloroprene	1. Acetylene, HCl	l.p. dimerization	65-75	2-5	$CuCl_2$, NH_4Cl,	
		l.p. hydrochlorination	25-50	-	$CuCl_2$	
Cresol (para)	1. p-cymene					
Cresylic Acids	1. Cracked naphtha, CO_2 or H_2SO_4	l.p. caustic extraction l.p. acid neutralization	-	-	-	Direct recovery

I-B. PRODUCTION OF COMMON INTERMEDIATE PETROCHEMICALS (Cont.)

PRODUCT	FEEDSTOCK	REACTION SEQUENCE	TEMP. ($^\circ$ C)	PRESSURE (psig)	CATALYSTS	REMARKS
Cumene	1. Propylene, benzene	v.p. alkylation	250	250-400	H_3PO_4	
		OR				
		l.p. alkylation	90-100		$AlCl_3$	
Cyclohexanol	1. Cyclohexane, air	l.p. oxidation	180	500	none	Cyclohexanone co-product
		OR				
		l.p. oxidation	155-160		Co	Cyclohexanone co-product
	2. Phenol, H_2	l.p. hydrogenation	150	50	Pd	
Cyclohexanone	1. Cyclohexanol	v.p. or l.p. dehydrogenation	-	-	v.p. - Zn, Fe l.p. - Ni	
	2. Phenol, H_2	l.p. hydrogenation	120-128	~ 0	Pd	
	3. Cyclohexane, air					See processes # 1 & 3 under cyclohexanol
Dodecene	1. Propylene	tetramerization	95-140	~250	H_3PO_4	Adiabatic
		OR				
		tetramerization	90-110	500	H_3PO_4	Adiabatic
		OR				
		tetramerization	95-100	900	H_3PO_4	Isothermal
Dodecylbenzene	1. Dodecene, benzene	l.p. alkylation	45- 55	-	$Al\ Cl_3$	
		OR				
		l.p. alkylation	0- 10	-	HF	
Epichlorohydrin	1. Propylene, Cl_2, lime	v.p. chlorination to allyl chloride	500-530	10- 15		
		l.p. chlorination to glycerol chlorohydrin	25 - 35	-	-	pH 0.5 - 2.0
		l.p. conversion w/lime	80- 90	-	-	

I-B PRODUCTION OF COMMON INTERMEDIATE PETROCHEMICALS (Continued)

PRODUCT	FEEDSTOCK	REACTION SEQUENCE	TEMP. (° C)	PRESSURE (psig)	CATALYSTS	REMARKS
Esters (all types)	1. Acid, alcohols	l.p. esterification	b.p.	-		
Ethanol	1. Ethylene, H_2SO_4	l.p. sulfation	60- 70	225-350	-	
		l.p. hydrolysis	b.p.			
	2. Ethylene, steam	v.p. hydration	300-570	1,000	H_3PO_4 or Tungsten oxide	
Ethyl Acetate	1. Acid, alcohols	See Esters				
	2. Acetaldehyde	l.p. conversion	0	-	Aluminum ethoxide, $AlCl_3$, ZnO	
Ethyl Benzene	1. C_8 reformate	Superfractionation	-	-		Direct recovery
	2. Ethylene, benzene	l.p. alkylation OR	90-100	~ 0	$AlCl_3$	Polyethyl benzene by-product
		v.p. alkylation	310	900	Silica-Al	Butyl-benzene polyethyl benzene by-product
Ethanolamines	1. Ethylene oxide, NH_3	l.p. ammonolysis	35- 40	-	-	All 3 ethanolamines formed as co-products
Ethyl Chloride	1. Ethylene, HCl	v.p. addition OR	175	250	$CuCl_2$, $ZnCl_2$ on alumina	
		l.p. addition	52	125	Al Cl_3 or BF_3 + H_3PO_4, or $AlCl_3$ + $FeCl_3$	
	2. Ethane, Cl_2	v.p. chlorination OR	390	110	Act. charcoal-photo chemical	HCl by-product
		v.p. chlorination	420	80	Thermal	HCl by-product

I-B PRODUCTION OF COMMON INTERMEDIATE PETROCHEMICALS (Continued)

PRODUCT	FEEDSTOCK	REACTION SEQUENCE	TEMP. (° C)	PRESSURE (psig)	CATALYSTS	REMARKS
Ethyl Chloride (Continued)	3. Ethanol, HCl	v.p. esterification OR			$ZnCl_2$	
		l.p. esterification	145	30	$ZnCl_2$	
Ethylene Dichoride	1. Ethylene, Cl_2	l.p. chlorination	46	75	$FeCl_3$	
	2. Ethylene, HCl, O_2	v.p. oxychlorination	285	0	$CuCl_2$ on alumina	
Ethylene Glycol	1. Ethylene oxide, H_2O	l.p. hydration OR	50-70	-	H_2SO_4	Di & triethylene glycol by-products
		l.p. hydration (Thermal)	195	200	None	
	2. Formaldehyde, CO, Methanol, H_2	l.p. reaction of CO and HCHO	150-225	7,300-14,700	HCl or H_2SO_4	Di & triethylene glycol by-products
		l.p. esterification	210-220	11,700-13,200	H_2SO_4	Alternate steps
		v.p. hydrogenation	210-215 225	427 565	CuO, ZnO, chromia MgO, CuO	
Ethylene Oxide	1. Ethylene, Cl_2, lime	l.p. chlorohydronation	20-35	variable		
		l.p. saponification with lime	96-102	0-10		pH 8-9
	2. Ethylene, air or O_2	v.p. oxidation	240-290		Ag	Feed purity requirements vary
2-Ethyl Hexanol	1. n-Butyraldehyde, H_2	l.p. aldolization	5-25	-	Aqueous caustic	
		l.p. dehydration	95	-	Sodium acid phosphate	
		l.p. hydrogenation	200	-	Ni	

I-B PRODUCTION OF COMMON INTERMEDIATE PETROCHEMICALS (Continued)

PRODUCT	FEEDSTOCK	REACTION SEQUENCE	TEMP. (° C)	PRESSURE (psig)	CATALYSTS	REMARKS
Formaldehyde	1. Methanol, air	v.p. oxidation-dehydrogenation	600-660	-	Ag	
		OR				
		v.p. oxidation	300-400	-	MoO_3, Iron	
	2. Propane or butane, O_2	see Acetaldehyde Process # 3				
	3. Dimethyl ether, air	v.p. oxidation	450-500	0	Metallic oxides	
Fumaric Acid	1. Maleic acid	l.p. isomerization	-	-		Thermal conversion
Glycerol	1. Epichlorohydrin, caustic	l.p. hydrolysis	150			NaOH, Na_2CO_3 used
	2. Acrolein, isopropanol, H_2O_2	v.p. reduction to allyl alcohol	350-450	-	MgO + ZnO	Acetone by-prod.
		l.p. reaction w/H_2O_2	90- 98	-	Sulfonic acids	
	3. Propylene oxide, Cl_2 or H_2O_2	v.p. isomerization to Allyl alcohol	280		$Li_3 PO_4$	
		AND				
		l.p. chlorination to glycerol chlorohydrin	-	-	-	
		l.p. conversion to epichlorohydrin				
		See process #1 above				
		OR				
		See process #2				
Hexamethylene Diamine	1. Adiponitrile, H_2	l.p. hydrogenation	100-135		Co sometimes + Cu	Fixed bed process

I-B PRODUCTION OF COMMON INTERMEDIATE PETROCHEMICALS (Continued)

PRODUCT	FEEDSTOCK	REACTION SEQUENCE	TEMP. (° C)	PRESSURE (psig)	CATALYSTS	REMARKS
Hydrogen Cyanide	1. Methane, NH_3, O_2	v.p. ammoxidation	950-1,000	-	Pt, Rhodium	
	2. Methane, NH_3	v.p. non-oxidative reaction	1,200-1,300	-	Pt	
Hydrogen Peroxide	1. Isopropanol, O_2	l.p. oxidation	90-140	200-300	H_2O_2 (autocatalytic)	Acetone co-product
Isophthalic Acid	1. m-Xylene, air	l.p. oxidation	190-200	to maintain l.p.	Mn acetate, NH_4Br	
	2. m-Xylene, NH_3, sulfur	l.p. oxidation	315-360	2,500-6,000	None	High mole ratio H_2O: xylene required
Isoprene	1. Isopentene	v.p. dehydrogenation (alternates)	620-675 500-675 595-675 650	~ 0 ~ 0 ~ 0 ~ 0	Fe_2O_3+Cr_2O_3+K_2CO_3 Mg-Fe oxide Ca-Ni phosphate Chromia-alumina	All procedures produce Complex C5 mixture as by-product
	2. Isopentane	v.p. dehydrogenation (one step)	600-650	-11.7	Chromia-alumina	"
	3. Propylene	l.p. dimerization v.p. isomerization v.p. pyrolysis (demethanization)	150-250 150-300 650-800	300 - -	Tripropyl aluminum acid HBr	"
Isopropanol	1. Propylene,	l.p. sulfation l.p. hydrolysis	60-70 b.p.	300-400 0	- -	
	2. Propylene, water	v.p. hydration	180-260	352-940	-	
	OR	OR				
	Propylene, steam	v.p. hydration	300	1,000	H_3PO_4 or tungsten oxide	

I-B PRODUCTION OF COMMON INTERMEDIATE PETROCHEMICALS (Continued)

PRODUCT	FEEDSTOCK	REACTION SEQUENCE	TEMP. (^{o} C)	PRESSURE (psig)	CATALYSTS	REMARKS
Maleic Anhydride	1. Benzene, air	v.p. oxidation	400-450	-	V_2O_5, MoO_3	Recovery by water scrubbing and dehydration
	2. Butenes, air	v.p. oxidation	350	-	MoO_3, V_2O_5	
Melamine	1. Urea	v.p. decomposition	350	-	None	
		v.p. conversion (catalytic)	400-450	-	-	
		OR				
		v.p. conversion (catalytic one step)	-	103-132	-	
Methacrylates	1. Acetone, HCN, alcohol, H_2SO_4	l.p. cyanhydrin formation	< 25	-	Alkaline	
		l.p. sulfation	80	-	-	
		l.p. rearrangement	125	-	-	
		l.p. esterification	90	-	-	
	2. Isobutene, alcohol	l.p. oxidation	5	-	N oxides, HNO_3 ammonium vanadate	
		l.p. dehydration l.p. esterification	-	-		
Methanol	1. CO, H_2	v.p. hydrogenation	350-375	3,665-14,685	CuO or ZnO	By-products: dimethylether, higher alcohols
	2. Natural gas, steam, CO_2 or CO_2,H_2	v.p. reforming	-		None	
		v.p. conversion	-	4,300	-	
	3. Butanal Propane, air	v.p. oxidation	430-530	100-300	None	Co-products acetaldehyde, formaldehyde, acetone, misc. oxygenated HC
Methyl Chloride	1. Methanol, HCl See Processes 1 & 3 for carbontetrachloride	v.p. hydrochlorination or l.p.	-	-	-	

I-B PRODUCTION OF COMMON INTERMEDIATE PETROCHEMICALS (Continued)

PRODUCT	FEEDSTOCK	REACTION SEQUENCE	TEMP. (° C)	PRESSURE (psig)	CATALYSTS	REMARKS
Methyl Ethyl Ketone	1. Sec-Butanol, H_2	v.p. dehydrogenation	380	~ 0	ZnO or Cu, Ni	
		OR				
		l.p. dehydrogenation	150	-	Ni	
	2. n-Butylene, Air or O_2	l.p. oxidation	20-100	-	$PdCl_3$, $CuCl_2$	
	3. By product in acetic acid process #3					
Methyl Isobutyl Carbinol	1. Acetone, H_2	l.p. adol condensation	5-25	~ 0	Caustic	
		l.p. dehydration	95	-	Sodium acid phosphate	
		v.p. hydrogenation	200	~ 0	Cu or Ni on pumic	By-product Methyl isobutyl ketone
Methyl Isobutyl Ketone	1. Acetone, H_2	Same as process for methyl isobutyl carbinol	-	-		By-product methyl isobutyl carbinol
Nitrobenzene	1. Benzene, HNO_3	l.p. nitration	35- 70	~ 0	H_2SO_4	Continuous or batch process
Nitroparaffins	1. Propane, HNO_3	v.p. nitration	400-425	-	Thermal	Mixed nitroparaffins formed
Nonene	1. Propylene	Trimerization - same as process for Dodecene				
Oxo Alcohols	1. Olefins, CO, H_2	l.p. hydrocarboxylation	130-175	1,500-4,000	Cobalt	
		l.p. or v.p. hydrogenation	100-150	575-1,160	hydrocarboxyl	
Pentaerythritol	1. Formaldehyde, Acetaldehyde	l.p. condensation-reduction 2 stages	30-45 55	- -	$Ca(OH)_2$ or NaOH, sometimes Cu	pH 9.0-9.5

I-B PRODUCTION OF COMMON INTERMEDIATE PETROCHEMICALS (Continued)

PRODUCT	FEEDSTOCK	REACTION SEQUENCE	TEMP. (° C)	PRESSURE (psig)	CATALYSTS	REMARKS
Phenol	1. Benzene, Cl_2,	l.p. chlorination	60- 70	-	$FeCl_3$	By-products: dichlorobenzene, diphenyl, diphenyl oxide
	NaOH	l.p. hydrolysis	370-400	4000		
		l.p. acidification	-	-		
	2. Benzene, H_2SO_4,	l.p. sulfonation	-	-		
	NaOH,	l.p. neutralization w/ Na_2SO_3 and lime	-	-		
	Lime, Na_2SO_3	l.p fusion w/NaOH	335-340	-	-	By-product: sodium sulfite
		l.p. acidification	-	-	-	
	3. Benzene, air, HCl	v.p. oxychlorination	250-270	-	oxides of Al, Cu, Fe	Polychlorinated benzene by-products
		v.p. hydration	480-500	-	$Ca_3(PO_4)_2$	
	4. Cumene, air	l.p. oxidation	110-130	~ 0	Cu porphyrins	Main by-product: acetone minor: methyl styrene, acetophenone
		l.p. fission	45- 65	~ 0	H_2SO_4	
	5. Toluene, air, steam	l.p. oxidation to benzoic acid	121-176	30	Co	
		l.p. oxidation-hydrolysis	221-243	~ 0	Cu + Mn or Mg	
	6. Benzene, air	v.p oxidation	500	-	Co or $AgNO_3$ or V_2O_5	
	7. Cyclohexane, air, H_2	l.p. oxidation				
		l.p. dehydrogenation			Pt	Benzene can be hydrogenated to cyclohexane as alternate scheme
Phthalic Anhydride	1. Naphthalene, air	v.p. oxidation OR	400-500	-	V_2O_5	Fixed bed
	2. o-Xylene, air	v.p. oxidation Same as #1 but w/catalyst variations OR	350-385	-	V_2O_5+K	Fixed or fluidized bed

I-B PRODUCTION OF COMMON INTERMEDIATE PETROCHEMICALS (Continued)

PRODUCT	FEEDSTOCK	REACTION SEQUENCE	TEMP. (° C)	PRESSURE (psig)	CATALYSTS	REMARKS
Phthalic Anhydride (Cont.)		l.p. oxidation	190-200	to maintain l.p.	Br, Mn salts	
Propylene Glycol	1. Propylene oxide, H_2O	l.p. hydration	50- 70		H_2SO_4	Dipropylene & monopropylene glycols as by-products
Propylene Oxide	1. Propylene, Cl_2, H_2O, lime	l.p. chlorohydrination	35	0	-	By-prod: propylene dichloride, chloroisopropyl ether
		l.p. dehydrochlorination	90-b.p.	0	-	
	2. Butane/Propane, air	See Acetaldehyde process #3	-	-	-	Occurs as by-product
Styrene	1. Ethylbenzene	v.p. dehydrogenation	520		ZnO or Mg & Fe oxides	
Terephthalic Acid	1. p-Xylene, HNO_3	l.p. oxidation	200	400		
	2. p-Xylene, air	l.p. oxidation	190-200	to maintain l.p.	Mn acetate, NH_4Br	
	3. p-Xylene, sulfur	l.p. oxidation	315-360	2,500-6,000	None	Aqueous NH_3 solvent
	4. p-Xylene, air, Methanol	l.p. oxidation	140-160	200	Co toluate	
		l.p. esterification w/ methanol	b.p.	-	HCl	
		l.p. oxidation	200-215	-	Co toluate	
	5. Potassium phthalate, CO_2	l.p. isomerization	380-420	720-1,455	Cd salts	
	6. Toluene, Formaldehyde, lime, HNO_3	l.p. chloromethylation w/	70	-	-	
		l.p. saponification w/lime	125	-	-	
		l.p. oxidation w/HNO_3	160-180	280	-	o-Phthalic acid by-product
		l.p. esterification	-	-	-	

I-B PRODUCTION OF COMMON INTERMEDIATE PETROCHEMICALS (Continued.

PRODUCT	FEEDSTOCK	REACTION SEQUENCE	TEMP. (° C)	PRESSURE (psig)	CATALYSTS	REMARKS
Terephthalic Acid (Continued)	7. Potassium benzoate	v.p. conversion	410-430	132-205	Cd	Benzene by-prod.
	8. Potassium ortho or isophthalate	v.p. conversion	410-430	29-103	Cd	-
Tetrachloroethylene	1. Propylene, Cl_2	v.p. chlorinolysis	400-500	-	Thermal	CCl_4, HCl by-products
	2. Ethylene, Cl_2	v.p. chlorination	600-650	-	Thermal	HCl by-product
	3. Ethylene dichloride, Cl_2	v.p. chlorination - dehydrochlorination	-	-	-	HCl by-product
	4. Pentachloroethane	dehydrochlorination	-	-	-	"
	5. Carbon tetrachloride	decomposition	-	-	Thermal	
Toluene Diisocyanate	1. Toluene, chlorine, H_2 HNO_3, H_2SO_4	Nitration of toluene hydrogenation to dicimino-toluene phosgenation	140	-	-	HCl, 2,6-diisocyanate by-products
Urea	1. CO_2, NH_3	v.p. carbonate formation dehydration	140-150 160-200	2,780-4,000 1,900-2,180	Thermal	
Vinyl Acetate	1. Acetic acid, acetylene	v.p. esterification	170-200	-	Zn Acetate	Exothermic reaction
	2. Acetic anhydride Acetaldehyde	l.p. formation of ethylidene diacetate	110-120	-	H_2SO_4	
		l.p. decomposition	-	-	Benzene sulfonic acid	Acetic anhydride solvent
Vinyl Chloride	1. Ethylene dichloride	v.p. dehydrochlorination	500	7-15	-	HCl by-product
	2. Acetylene, HCl	v.p. hydrochlorination	100-180	-	$HgCl_2$	

I-B PRODUCTION OF COMMON INTERMEDIATE PETROCHEMICALS (Continued)

PRODUCT	FEEDSTOCK	REACTION SEQUENCE	TEMP. (° C)	PRESSURE (psig)	CATALYSTS	REMARKS
Vinylidene Chloride	1. Vinyl chloride or dichloroethane, lime or NaOH	chlorination to 1, 1,2-trichloroethane		-	-	
		l.p. dehydrochlorination w/lime or NaOH	98- 99	-	-	By products: NaCl w/NaOH, HCl w/lime

v.p. vapor phase
l.p. liquid phase
(-) indicates data not available
b.p. boiling point

APPENDIX II

Major Petrochemical Products and Wastes Profile

(Reference VIII - 7)

I-C SOME PROCESSES FOR THIRD-GENERATION PETROCHEMICALS
(Polymers, final products, etc.)

PRODUCT	FEEDSTOCK	REACTION SEQUENCE	TEMP. (° C)	PRESSURE (psig)	CATALYSTS	REMARKS
Ammonia	1. Synthesis gas	v.p. shift conversion (catalytic) (2-stages)	340-455 205-260	- -	- -	1st stage 2nd stage
		v.p. gas purification	-	-	-	CO_2 removed
		v.p. synthesis (catalytic)	-	2,000-9,000	-	-
Butyl Rubber	1. Isobutylene, isoprene, methyl chloride	l.p. polymerization (catalytic)	-95	0	-	
		l.p. purification	-	0	-	Hydrocarbons recycled
Carbon Black	1. Aromatic oils, air, fuel gas	v.p. cracking (thermal)	1,320-1,600	0	none	CH_4, acetylene, CO_2, CO, water by-products
Melamine	1. Urea	v.p. decomposition	350	-	-	NH_3 is used as carrier gas
		v.p. conversion (catalytic)	400-450	0-130	-	
Nitrile Rubber	1. Butadiene, acrylonitrile	l.p. polymerization (catalytic)	<27	0	-	Reaction takes place in soapy water sol.
Neoprene	1. Chloroprene	l.p. emulsification	38	0	none	Regulating chemicals added
		l.p. polymerization (catalytic)	38	0	-	
Cis-Polybutadiene	1. 1,3-Butadiene Benzene, antioxidant, modifier, short-stop agent	l.p. polymerization	20-50	0	Al-organic, Co	
		OR				
		l.p. polymerization	5-40	0	Aluminum chlorohydrile etherate, AlI_3, $TiCl_4$	
Polybutenes (ISO)	1. i-Butylene	l.p. polymerization	-	0	$AlCl_3$	Light polymers, C4 hydro-carbon by-product

I-C SOME PROCESSES FOR THIRD GENERATION PETROCHEMICALS (Continued)
(Polymers, final products, etc.)

PRODUCT	FEEDSTOCK	REACTION SEQUENCE	TEMP. (° C)	PRESSURE (psig)	CATALYSTS	REMARKS
Polycarbonates	1. Bisphenol-A, phosgene, pyridine, solvent	l.p. polymerization	38	0	-	Pyridine hydrochlorine by-product
Polyethylene (low density)	1. Ethylene	l.p. polymerization (catalytic)	150-250	14,600-32,500	peroxides	Oxygen is Initiator
Polyethylene	1. Ethylene	l.p. polymerization OR l.p. polymerization OR l.p. polymerization	50-75 150-180 200-260	25-150 500 500-1,000	Al-alkyl, $TiCl_4$ $Cr_2\ _3$ on SiO_2-Al_2O_3 MoO_2 on Al_2O_3	HC suspension medium HC suspension medium HC suspension medium
Polypropylene	1. Propylene	l.p. polymerization	80-95	25-50	Al-alkyl, $TiCl_3$	HC suspension medium
Polyisoprene	1. Isoprene, aliphatic hydrocarbon	l.p. polymerization	5-40	0	$TiCl_4$, Al-organic	-
Polyolefin Copolymers; Ethylene-Propylene	1. Propylene, ethylene	l.p. polymerization	-	500-1,000	metal oxides (Al, V)	-
Styrene-Butadiene	1. Styrene, butadiene (oil/carbon black)	l.p. polymerization - cold hot	 5 27	 0 0	 - -	Soap solution used as solvent
Sulfur	1. Acid gas (H_2S)	v.p. partial oxidation v.p. reaction of SO_2 with H_2S OR v.p. oxidation	- - -	- - -	None None Bauxite	- - SO_2 by-product

v.p. vapor phase

l.p. liquid phase

(-) indicates data not available

ACETALDEHYDE

Present Producers	Capacity*
Celanese, Bay City, Texas	210
Celanese, Bishop, Texas	200
Celanese, Clear Lake, Texas	195
Celanese, Pampa, Texas	10
Eastman, Kingsport, Tennessee	200
Hercules, Parlin, New Jersey	250
Publicker, Philadelphia, Pa.	80
Union Carbide, various locations	650
Others	22
Total	1,832

*million pounds

Production

1968: 1,600 million pounds
1973: 1,950 million pounds

Uses

Acetic acid and anhydride, n-butanol, 2-ethylhexanol

Process

Acetaldehyde is produced from

1) Hydration of acetylene

$$C_2H_2 + H_2O \longrightarrow CH_3CHO$$

2) Oxidation of Ethyl Alcohol

$$C_2H_5OH + 1/2\ O_2 \longrightarrow CH_3CHO + H_2O$$

3) Oxidation of lower paraffin (propane and butane)

4) Oxidation of ethylene via the Wacker process

$$CH_2CH_2 + PdCl_2 + H_2O \longrightarrow CH_3CHO + Pd + 2HCl$$

$$Pd + 2HCl = 1/2O_2 \longrightarrow PdCl_2 + H_2O$$

The Wacker process is the only major process being installed today and it is anticipated that future expansions will be based on this route.

Waste Problems

A typical Wacker process discharges about 1,200 gallons per ton of product. The composition of the waste stream is primarily chlorinated aldehydes with a COD in the order of 10,000 mg/l. This is based on a yield of 95 percent. The waste is difficult to treat biologically unless it is diluted with others waters. In addition, it is quite acid and runs around pH two. It is to be noted that several facilities handle these wastes by means of a deep well rather than by biological treatment.

Reduction in Waste Loading by Process Change

It is possible by means of a rather simple still design change to concentrate the waste stream so as to reduce the discharge to 150-200 gallons/ton of product. No reduction in organic loading is produced and this approach is only practiced in those cases where deep well disposal or incineration is planned. The process change costs about $50,000 in a typical 200,000,000 pounds/year facility.

The only possible means of reducing the organic load center around recovery and use of the chlorinated aldehydes, dechlorination of the aldehydes or improvements in yield. The latter is where emphasis is placed. It is expected that the average yield will reach 97 percent in five years thereby reducing organic loading by about 40 percent.

ACETIC ACID AND ANHYDRIDE

Acid Producers	Capacity*
Borden, Geismer, La.	100
Celanese, Bishop, Texas	200
Celanese, Pampa, Texas	500
Eastman, Kingsport, Tennessee	325
Hercules, Parlin, New Jersey	40
Publicker, Philadelphia, Pa.	80
Union Carbide, Brownsville, Texas	500
Union Carbide, S. Charleston, W. Va.	140
Union Carbide, Texas City, Texas	100
Total	1,985

*million pounds/year does not include by-product and fermentation acetic acid which amounts to 100,000,000 pounds.

Production

1968: 1,700 million pounds
1973: 2,500 million pounds

Uses

Cellulose acetate, vinyl acetate, acetic esters, chloroacetic acid

Process

Acetic acid is produced:

1) by oxidation of acetaldehyde,
2) from ethanol,
3) by LPG oxidation (liquified petroleum gas), and
4) from methanol and carbon monoxide.

The most popular technique in use is the oxidation of acetaldehyde while production from ethanol is only of minor importance. The Reppe method, from methanol and CO, is the newest method (developed by BASF) and appears to be gaining favor in this country. In the future it is expected that processes based on acetaldehyde and methanol will predominate in the production of acetic acid and anhydride.

Waste Problems

LPG oxidation results in the production of substantial amounts of other acids such as formic and propionic which must be disposed of by incineration, resale or biological oxidation. Unfortunately, resale of these materials does not appear to be practical because the markets for these chemicals are quite limited. Waste flow for this system is in the order of 1,000 gallons/ton of product and the organic concentrations are in excess of 30,000 mg/l. In some operations, the stream is neutralized (it usually runs at pH 4) with caustic and the sodium salts of the acid are recovered. Treatment by a number of means is routine. Biological modes are quite adequate.

Oxidation of acetaldehyde also produces higher acids and other oxidized species in quantities somewhat less than produced by LPG oxidation. Water flows are of the same magnitude, but organic load is about 50 percent of the load generated by the oxidation of LPG.

In the Reppe process, about 80 pounds of organics (50 percent propionic acid and 50 percent higher organics) are produced in the liquid waste stream per ton of product. The liquid stream amounts to about 50 gallons per ton of product including drains.

Reduction in Waste Loading by Process Change

The changes in process do not appear to change the nature of the wastes generated by the production of acetic acid or the quantity of the waste. Further, the amounts and character of the waste would not appear to create serious waste treatment problems or expenditures.

There will be improvements in the yield picture which will certainly assist in reducing the waste management problems, but it is not anticiated that any changes will radically change the waste situation.

ACETONE

Producers	Capacity*
Allied, Frankford, Pa.	150
Celanese, Bishop, Texas	35
Chevron, Richmond, Calif.	35
Clark, Blue Island, Illinois	30
Eastman, Kingsport, Tennessee	60
Enjay, Linden, New Jersey	110
Hercules, Gibbstown, New Jersey	30
Monsanto, Alvin, Texas	75
Shell, Dominquez, Calif.	150
Shell, Houston, Texas	210
Shell, Norco, La.	100
Skelly, El Dorado, Kansas	30
Union Carbide, Institute, W. Va.	120
Union Carbide, Bound Brook, N. J.	90
Union Carbide, Texas City, Texas	130
Union Carbide, Whiting, Indiana	120
Total	1,475

*millions of pounds per year

Production

1968: 1.3 billion pounds
1973: 1.8 billion pounds

Uses

Methyl isobutyl ketone and carbinol, Methyl acrylate, bisphenol A, paint, lacquer and varnish solvent, cellulose acetate solvent.

Processes

Currently there are three major processes utilized for the production of acetone.

There are

a) dehydrogenation of isopropyl alcohol,

$$(CH_3)_2\ CHOH \longrightarrow (CH_3)_2\ CO + H_2$$

b) by-product from the production of phenol from cumene, and

$$(C_6H_5)\ (C_3H_7) + O_2 \longrightarrow C_6H_5OH + C_3H_6O$$

c) direct oxidation of propylene.

$$CH_3CH = CH_2 + 1/2O_2 \longrightarrow CH_3COCH_3$$

It is expected that a major portion of the acetone will continue to be produced from cumene as a phenol by-product. It seems likely that direct oxidation of propylene will gain asendency relative to the production from isopropyl alcohol.

Waste Problems

The processes based on isopropyl alcohol dehydration produce about 200-250 pounds of organics per ton of product. These consist of still bottoms (0.5 percent organics) principally. The nature of the organics is somewhat complex but may include acetone, unreacted alcohol and higher polymeric species. The amount of wastewater depends in part upon the amount of cooling water utilized as well as the frequency of equipment cleaning. It is also important to note that the process utilizes either metallic copper or zinc acetate as a catalyst and catalyst cleanup could put significant amounts of these materials into the water course or to treatment.

Direct oxidation results in a yield of 93 percent which in turn produces less than 80 pounds per ton of product as an organic load within the system. Water load varies, but exclusive of cooling water, amounts to about 750 gal/ton. The regeneration of the cupric chloride catalyst may cause difficulty.

Waste Reduction by Process Change

The utilization of direct oxidation will greatly reduce the amount of organic discharge both when directly compared with isopropyl alcohol based processes and when considering the additional waste generated by the production of isopropyl alcohol. Therein lies another key factor in the evaluation of trends in the chemical industry. The desire to reduce the number of processing steps both to reduce direct operating costs and to increase yield generally results in greatly reduced waste loads.

It is possible through careful control and operation of the still to greatly reduce the amount of acetone in the still bottoms. These costs are generally minor relative to the value of the recovered acetone but must be the result of a conscious management effort.

ACETYLENE

Producers	Capacity*
Diamond, Deep Park, Texas	40
Dow, Freeport, Texas	15
Monochem, Geismer, La.	165
Monsanto, Texas City, Texas	100
Rohm and Haas, Deep Park, Texas	35

Producers	Capacity*
Tenneco, Houston, Texas	100
Union Carbide, various locations	150
Total	650

*millions of pounds per year

Production

1968: 610 million pounds
1973: 630 million pounds

Uses

Vinyl chloride, vinyl acetate, neoprene, acrylates and acrylonitriles

Processes

Acetylene is produced from two major sources in the United States. About 50 percent of the acetylene is produced by the reaction of calcium carbide and water.

$$CaC_2 + 2H_2O \longrightarrow C_2H_2 + Ca(OH)_2$$

The second process involves the partial oxidation of natural gas.

$$2CH_4 \longrightarrow C_2H_2 + 3H_2$$

Other approaches involve the pyrolysis route as shown below as typified by the Wulff process,

$$C_4H_{10} \longrightarrow C_2H_2 + C_2H_4 + CO$$

$$C_2H_4 \longrightarrow C_2H_2 + H_2$$

$$2CH_4 \longrightarrow C_2H_2 + 3H_2$$

It is unlikely that many changes will occur with regard to the production of acetylene in this country unless someone comes up with a process with greatly reduced production costs which would have the effect of bringing the cost of acetylene close to the cost of ethylene. It this does not occur, it will not be possible for acetylene to maintain many markets in the face of ethylene.

Waste Problems

The major waste associated with the production of acetylene from calcium carbide is the lime slurry residue.

However, the hydrocarbon processes do generate large amounts of water borne wastes. These quantities are quite variable and depend upon the feedstock, the degree of pyrolysis, the ratio of acetylene to olefins produced, etc.

The wastes arise from the gas cooler and the scrubbing of the higher concentrations of tars and oils and are quite difficult to treat in conventional biological treatment facilities. Incineration is usually used to burn soot oil, soot water, and organic tars.

Waste Reduction by Process Change

The key factor in waste management in the production of acetylene from hydrocarbons centers around the control of the cracking furnaces to maximize the production of valuable products. Improvements in the difficult-to-optimize reaction system are keys to the success of the process but quite difficult to improve. Since efficiencies have been known to run as low as 40-50 percent, it is not surprising that efficiency improvement is vital to the process. This is the key process change which can be implemented and returns from this operation are tremendous relative to production of costs. Further, recoveries of waste products in burnable form is also vital to the effective operation of the unit. In some operations, a solvent is used to recover the acetylene. Solvent losses may be significant and add to the dimensions of the waste treatment problem. Careful selection of the solvent, and improved design of the vacuum stripper should assist in reducing solvent losses.

ACRYLATES

Producers	Capacity*
Celanese, Pampa, Texas	45
Dow, Freeport, Texas	40
Goodrich, Calvert City, Kentucky	5
Minnesota Mining, St. Paul, Minn.	3
Rohm and Haas, Deer Park, N. J.	200 (a)
Union Carbide, Taft, La.	200 (b)
Union Carbide, Institute, W. Va.	50 (b)
Total	543

*million of pounds/year

(a) 120 million pounds to be added by 1969
(b) Taft facility completed by October, 1968;
    Institute may be retired

Production

1968: 240 million pounds
1973: 400 million pounds

Uses

Paint latices, textiles, acrylic specialities, acrylic fibers

Processes

The major process involved in the production of acrylates is the oxidation of acetaldehyde.

Waste Problems

Waste streams associated with this operation are generally composed of polymerization and degradation.

The flow rate is about 1,500 gallons per ton of product with organic concentrations about 10-20,000 mg/l. Yields in this process could be improved thereby reducing waste problems. A number of waste streams and gas vents are often incinerated. Extension of this practice would reduce the amount of wastewaters to be treated.

Waste Reduction by Process Change

Considerable efforts are underway to improve yields and this should result in lower wastewater discharge.

AMMONIA

Major Ammonia Producers (600 TPD and up)

Producer	Capacity*
Air Products, Michoud, La.	600
Allied, Geismar, La.	1,000
Allied, Hopewell, Va.	1,000
Apple River, E. Dubuque, Illinois	700
American, Texas City, Texas	2,100
American Cyanamid, Avondale, La.	1,000
Arkla, Helena, Arkansas	600
Borden, Geismar, La.	900
Central Farmers, Donaldsonville, La.	1,000
Chevron, Pascagoula, Miss.	1,500
Coastal, Yazoo, Miss.	1,000
Collier, Brea, California	750
Collier, Cook Inlet, Alaska	1,500
Commercial Solvents, Sterlington, La.	1,000
Consumers, Fort Dodge, Iowa	600
Continental, Blytheville, Arkansas	1,000
duPont, Beaumont, Texas	1,000
duPont, Belle, W. Va.	1,000
Farmland, Dodge City, Kansas	600
First Mississippi, Donaldsonville, La.	1,000
First Nitrogen, Donaldsonville, La.	1,000
Gulf, Borger, Texas	1,000
Mobil, Beaumont, Texas	750
Monsanto, Luling, La.	1,000

Producer	Capacity*
Olin-Mathieson, Lake Charles, La.	1,400
Phillips, Beatrice, Neb.	600
Sinclair, Ft. Madison, Iowa	1,000
Terra, Port Neal, Iowa	600
U. S. Steel, Clairton, Pa.	1,150
Valley Nitrogen, El Centro, Calif.	600
Total	29,550

*Tons/Day

Production

1968: 14,200,000 tons/year
1973: 20,000,000 tons/year

Uses

Fertilizers, urea, nitric acid

Processes

Ammonia is produced from syhthesis gas ($CO + H_2$) under conditions of relatively high temperatures and high pressure. Synthesis gas is produced primarily by the steam reformation of natural gas or other hydrocarbon sources as shown below:

$$CH_4 + H_2O \longrightarrow CO + 3H_2$$

During the reformation, air is added to provide additional energy for the endothermic reformation reaction. The air also provides N_2 for ammonia formation. The CO is converted to CO_2 and removed. Conversion to ammonia then takes place:

$$N_2 + 3H_2 \longrightarrow 2NH_3$$

The major change in processing technology which has taken place recently has been the development of large single train ammonia plants of capacities as high as 1,500 tons/day. This trend is expected to continue. These plants produce large point source concentrations of ammonia and carbon dioxide. However, these large streams have made the recovery of ammonia practical.

Waste Problems

The major streams arising from an ammonia plant are process condensate and site drains. The flow and waste produce loads are as listed below:

Flow (Gals/Ton of product)	300
NH_3 (Lbs/Ton)	0.1

NH_4HCO_3 (Lbs/Ton)	0.1
MEA (Monoethanolamine) (Lbs/Ton)	0.2
CO_2 (Lbs/Ton)	0.7

Normal practice in this country is to either strip the ammonia or to release the discharge untreated although it is anticipated that this practice cannot be continued in the future.

Waste Reduction by Process Change

It is possible to reduce the ammonia loss by some 60 percent by adjusting pH and airstripping. About 0.1 pounds of NaOH is added per ton of product. This is normal practice. It is possible to remove greater amounts of NH_3 (90-95 percent) by increasing the air flow to perhaps 500-1,000 scf/gal. Following the normal industry practice cost of the stripper and condenser is about $60,000 for a 1,200 ton/day plant. The cost of removing additional quantities of ammonia have not been calculated since no plants practicing this extreme approach have ever been built.

BENZENE

Producers	Capacity*
Allied, Winnie, Texas	4
Amoco, Texas City, Texas	15
Ashland, N. Tonawanda, N. Y.	10
Ashland, Catlettsburg, Ky.	20
Atlantic-Richfield, Wilmington, Calif.	18
Atlas, Shreveport, La.	10
Chevron, El Segundo, Calif.	25
Chevron, Richmond, Calif.	10
Continental, Lake Charles, La.	6
Continental, Ponca City, Okla.	6
Cosden, Big Spring, Texas	9
Crown Central, Houston, Texas	38
Dow, Bay City, Mich.	20
Dow, Freeport, Texas	30
Enjay, Baton Rouge, La.	24
Enjay, Baytown, Texas	55
Gulf, Philadelphia, Pa.	27
Gulf, Port Arthur, Texas	32
Hess, Corpus Christi, Texas	30
Leonard, Mt. Pleasant, Mich.	3
Marathon, Texas City, Texas	6
Mobil, Beaumont, Texas	30
Monsanto, Alvin, Texas	65
Phillips, Sweeny, Texas	22

Producers	Capacity*
Pontiac, Corpus Christi, Texas	9
Shell, Houston, Texas	31
Shell, Odessa, Texas	20
Shell, Wilmington, Calif.	15
Shell, Wood River, Illinois	30
Signal, Houston, Texas	22
South Hampton, Silsbee, Texas	6
Sun, Marcus Hook, Pa.	15
Sunray DX, Tulsa, Oklahoma	22
Suntide, Corpus Christi, Texas	25
Tenneco, Chalmette, La.	15
Texaco, Port Arthur, Texas	30
Union Carbide, S. Charleston, W. Va.	10
Union Atlantic, Nederland, Texas	18
Union Oil, Lemont, Illinois	22
Vickers, Potwin, Kansas	3
Total from Petroleum Feedstocks	809
Total from 18 Cokeoven Producers and 3 Tar Distillers	142
Grand Total	951
Cities Service, Lake Charles, La.	55
Coastal States, Corpus Christi, Texas	6
Gulf, Port Arthur, Texas	25
Southwestern, Corpus Christi, Texas	6
Texaco, Port Arthur, Texas	15
Total announced new capacity	107
Grand Total, all United States Capacity	1,058

*millions of gallons/year

Production

1968: 900 million gallons
1973: 1,350 million gallons

Uses

Styrene, phenol, cyclohexane, detergent, aniline, Maleic acid, DDT

Processes

About 60 percent of United States benzene is produced by recovery (together with toluene and xylenes) from refinery reformers while an additional 20 percent is produced from the dealkylation of toluene. Coal, tar, coke oven light oils, and ethylene drip oils account for the remainder. It is expected that refinery based benzene will grow more rapidly than other sources. Naphthalene is similar.

Waste Sources

The major sources of wastewater in the recovery of benzene, xylenes, and toluene from refinery reformate are two-fold. First, cooling waters tend to pick up between 50-200 ppm of COD in the form of aromatics because of heat exchanger leaks. The quantity and quality of wastewater arising from this source will depend upon the cooling system and will in general be associated with other cooling waters.

The aromatics are separated from the paraffins by extraction with aqueous diethylene glycol. Discarding of this solvent stream in order to control impurity buildup results in a waste stream containing aromatics and diethylene glycol. Here improvements in stripper design and careful control of blowdown from the solvent cycle will assist in greatly reducing wastewater discharges.

Waste Reduction by Process Change

This control is possible primarily by (1) close maintenance of heat exchangers, (2) yield improvements, and (3) stripper design.

BUTADIENE

Producers	Capacity*
Chevron, El Segundo, Calif.	16,000
Copolymer, Baton Rouge, La.	60,000
Dow, Freeport, Texas	45,000
El Paso, Odessa, Texas	45,000
Enjay, Baton Rouge, La.	75,000
Enjay, Baytown, Texas	33,000
Firestone, Orange, Texas	110,000
Goodrich-Gulf, Port Neches, Texas	160,000
Mobil, Beaumont, Texas	25,000
Monsanto, Alvin, Texas	50,000
PCI (Cities Service), Lake Charles, La.	80,000
Petro-Tex, Houston, Texas	275,000
Phillips, Borger, Texas	112,000
Shell, Torrance, Calif.	70,000
Sinclair, Channelview, Texas	121,000
Texas-U.S., Port Neches, Texas	160,000
Tidewater, Delaware City, Del.	10,000
UCC, Seadrift, Texas; Ponce, P.R.	105,000
Total	1,577,000

*Tons per year

Production

1968: 1.50 million tons
1973: 1.80 million tons

Uses

Styrene-butadiene rubber, polybutadiene rubber, adiponitrile, nitrile rubber, S-B and A-B-S plastics

Processes

Butadiene is produced from three major sources:

1) dehydrogenation of n-butylenes,
2) dehydrogenation of n-butane, and
3) as a by-product of ethylene production

It is anticipated that by-product production will increase rapidly because of the expected rapid increase in ethylene production.

Waste Problems

Waste flows from butadiene production facilities amount to some 100 gals/ton of product with waste compositions as follows (taken from one source only):

pH	8-9
TOC	100-200 mg/l
filtered COD	250-375 mg/l
suspended solids	200-500 mg/l
total solids	3,000-4,000 mg/l (sulfates and chlorides principally)

Waste Reduction Through Process Modification

Little information is available regarding possible process modifications.

BUTANOL

Producers	Capacity*
Celanese, Bishop, Texas	125
Continental Oil, Westlake, La.	5
Dow-Badische, Freeport, Texas	15
Eastman, Longview, Texas	60

Producers	Capacity*
Shell Chemical, Houston, Texas	50
Union Carbide, various locations	240
Total	495

*millions of pounds annually

Production

1968: 500 million pounds
1973: 620 million pounds

Uses

Glycolethers and amine resins, solvent, n-butyl acetate, plasticizers

Process

Butanol is produced by the oxidation of LPG or other petroleum streams.

Waste Problems

Waste streams arise primarily from the still discharges following the separation of various products together with wastes resulting from catalyst and vessel cleanouts. Cooling waters also contain considerable wastes. Wastewaters discharged amount to several hundred gallons per ton of product while organic discharges amount to 100-300 pounds/ton of product.

Waste Reduction by Process Change

The waste problems of this process involve the low efficiency and rather drastic conditions under which the reaction takes place. Improvements in yields and improvements in still efficiencies would improve the situation. Further provisions can be made for the collection and direct incinerations of still bottoms, vessel cleanout wastes, etc., without contamination of the wastewaters.

A number of waste streams may be either sent to additional strippers or vented to gas burners. The costs of such controls amount to some $250,000-$500,000 for an 80 million pound/year plant and will reduce the waste load by 25-50 percent.

CARBON MONOXIDE AND HYDROGEN (SYNTHESIS GAS)

See Ammonia

CARBON TETRACHLORIDE AND OTHER CHLORINATED HYDROCARBONS

Carbon Tetrachloride:

Producers	Capacity*
Allied, Moundsville, W. Va.	8
Diamond, Painesville, Ohio	35
Dow, Freeport, Texas	130
Dow, Pittsburg, Calif.	30
Dow, Plaquemine, La.	20
FMC-Allied, S. Charleston, W. Va.	200
Stauffer, Le Moyne, Alabama	85
Stauffer, Louisville, Ky.	70
Stauffer, Niagara Falls, N. Y.	125
Volcan, Wichita, Kansas	25
Total	728

*millions of pounds per year

Chloroform:

Producers	Capacity*
Allied, Moundsville, W. Va.	30
Diamond, Belle, W. Va.	20
Dow, Freeport, Texas	75
Dow, Pittsburg, Calif.	1
DuPont, Niagara Falls, N. Y.	15
Stauffer, Louisville, Ky.	75
Vulcan, Newark, N. J.	6
Vulcan, Wichita, Kansas	16
Total	238

*millions of pounds per year

Methylene Chloride:

Producers	Capacity*
Allied, Moundsville, W. Va.	50
Diamond, Belle, W. Va.	30
Dow, Freeport, Texas	85
Dow, Pittsburg, Calif.	20
DuPont, Niagara, Falls, N. Y.	60
Stauffer, Louisville, Ky.	70
Vulcan, Newark, N. J.	20
Vulcan, Wichita, Kansas	20
Total	355

*millions of pounds per year

Methyl Chloride:

Producers	Capacity*
Allied, Moundsville, W. Va.	17
Ancon, Lake Charles, La.	100
Dow, Freeport, Texas	100
Dow, Pittsburg, Calif.	20
Dow Corning, Midland, Michigan	10
Dow Corning, Carrollton, Kentucky	20
DuPont, Niagara Falls, N. Y.	76
Ethyl, Baton Rouge, La.	75
General Electric, Waterford, N. Y.	24
Vulcan, Newark, N. J.	2
Total	454

*millions of pounds per year

Production

	CCl_4	$CHCl_3$	CH_2Cl_2	CH_3Cl
1968:	700	200	265	240
1973:	900	300	400	370

Use

Fluorocarbons, solvents

Process

These chlorinated methanes are produced by the reaction of chlorine with methane and then are separated by fractionation. Carbon tetrachloride is also produced by the reaction of hydrogen chloride with carbon disulfide.

Waste Problems

The major waste stream results from the production of hydrogen chloride as a by-product of the reaction.

Waste Reduction by Process Change

The main need is for routes to the economic recovery of chlorine from hydrogen chloride or through the reuse of hydrogen chloride. A number of new oxychlorination processes have recently been developed which enable the user to utilize hydrogen chloride together with chlorine in a balanced facility. As an example, for the production of carbon tetrachloride:

$$CH_4 + 4Cl_2 \longrightarrow CCl_4 + 4HCl$$

$$CH_4 + 4HCl + 2O_2 \longrightarrow CCl_4 + 4H_2O$$

This approach eliminates the problem of hydrogen chloride but it does produce about 60 gallons of wastewater per ton of product which will contain minor amounts of chlorinated methanes and HCl. Further, these reactions often have an intermediate step involving copper chloride and small amounts of this catalyst will be released to the wastewater. Insufficient data is available to predict relative waste loads and economics. It is anticipated that process changes will substantially eliminate the HCl being generated in these operations.

CELLULOSE ACETATE

Producers	Capacity*
Celanese, various locations	450
DuPont, Waynesboro, Va.	60
Eastman, Kingsport, Tenn.	215
FMC, Meadville, Pa.	25
Total	750

Production

1968: 740 million pounds
1973: 850 million pounds

Uses

Fibers, cigarette filters, plastics

Processes

Reaction of wood pulp with acetic acid and anhydride to produce triacetate, hydrolysis to produce diacetate.

Waste Problems

Major waste sources arise from the stills used to recover acetic acid and acetone and other solvents. In addition, the wastes contain considerable amounts of degraded celluloses as well as phosphates (used as catalyst) and sulfuric acid (from spills). About 3-3.5 gallons of wastewaters are generated with a solid loading of 200 mg/l and a BOD of 1-3,000 mg/l depending upon the relationship of flake to fiber production.

Waste Reduction Through Process Change

There are numerous opportunities for waste reduction in cellulose acetate production. Among these are the following:

1) recovery and reuse of CA fines,
2) careful pH control in acetone stills,
3) control of vessel cleanout and acid spills,
4) improved operation of acetone and acetic acid stills, use of additional stills to improve recovery, and
5) higher yields on cellulose (wood pulp)

CYCLOHEXANE

Producers	Capacity*
Ashland, Catlettsburg, Ky.	30
Atlantic Richfield, Wilmington, Calif.	15
Commonwealth-Shell, Puerto Rico	30
Continental, Ponca City, Okla.	80
Continental, Lake Charles, La.	
Cosden, Big Springs, Texas	8
DuPont, Belle, W. Va.	15
DuPont, Orange, Texas	15

*millions of gallons per year

Producers	Capacity*
Eastman, Longview, Texas	3
Enjay, Baytown, Texas	40
Gulf, Port Arthur, Texas	33
Phillips, Borger, Texas	47
Phillips, Sweeny, Texas	53
Phillips, Puerto Rico	40
Pontiac, Corpus Christi, Texas	12
Signal, Houston, Texas	17
South Hampton, Silsberg, Texas	3
Texaco, Port Arthur, Texas	40
Union Oil, Smith's Bluff, Texas	33
Total	514

*millions of gallons per year

Production

1968: 310 million gallons
1973: 570 million gallons

Uses

Nylon 66, Nylon 6

Processes

About 30 percent of the cyclohexane produced in this country is produced from the fractionation of petroleum. The remainder is produced by the catalytic hydrogenation of benzene. This latter process will account for some 85 percent of the cyclohexane produced in the United States after 1970.

Waste Problems

Outside of spills, the only major source of water is the cooling water which amounts to 200-2,000 gallons/ton of cyclohexane and which may contain 50-200 mg/l of COD. In aromatics extraction, there are two major sources of wastewater, the extract water washing which contains aromatic hydrocarbons and the wastes from solvent degeneration which contain appropriate solvents. Both wastes may be minimized by the use of stripping columns.

Waste Reduction by Process Change

No forseeable changes in process will have any significant impact upon wastewater discharges except for the replacement of once-through cooling with cooling towers. However, once-through cooling is generally not utilized in cyclohexane facilities.

CUMENE

Producers	Capacity*
Amoco, Texas City, Texas	50
Ashland, Catlettsburg, Ky.	300
Chevron, Richmond, Calif.	80
Clark, Blue Island, Illinois	100
Coastal States, Corpus Christi, Texas	100
Dow, Midland, Michigan	10
Gulf, Philadelphia, Pa.	400
Gulf, Port Arthur, Texas	300
Hercules, Gibbstown, New Jersey	60
Marathon Oil, Corpus Christi, Texas	125
Monsanto, Alvin, Texas	130
Shell, Houston, Texas	80
Skelly, El Dorado, Kansas	80
Sunray DX, Corpus Christi, Texas	125
Texaco, Westville, N. J.	140
Total	2,220

*millions of pounds/year

Production

1968: 1.2 billion pounds
1973: 2.2 billion pounds

Uses

Phenol, acetone, α-methylstyrene

Process

The process for the production of cumene involves a phosphoric acid catalyzed alkylation of benzene with propylene. No significant change in this technology is anticipated in the near future.

Waste Problems

The principal waste streams from the manufacture of cumene are the process slops and the "cumene" bottoms which are a result of the recovery of cumene from the general process stream. This stream contains some 1-4 percent of the product stream. The quantity of water carrying the wastes depends largely upon the use of propane to control bed temperature.

Waste Reduction Through Process Change

Careful temperature control through propane injection may reduce the amount of by-products and reduce the amount of water required in the tower to control this highly exothermic reaction.

ETHANOL

Producer	Capacity*
Synthetic (Ethylene)	
Enjay, Baton Rouge, La.	60
Eastman, Longview, Texas	25
Publicker, Philadelphia, Pa.	25
Shell, Houston, Texas	40
Union Carbide, S. Charleston, W. Va.	60
Union Carbide, Texas City, Texas	100
USI, Tuscola, Illinois	53

*millions of wine gallons annually, 190 proof alcohol

Producer	Capacity*
Other Industrial	
Ga-Pacific, Bellingham, Wash.	
Hercules, Hopewell, Va.	

Producer	Capacity*
Publicker, Philadelphia, Pa., other	20
Total	383

*millions of wine gallons annually, 190 proof alcohol

Production

1968: 299 million gallons
1973: 330 million gallons

Uses

Acetaldehyde, solvent, other chemicals

Process

Two processes are in use to produce ethanol from ethylene. The first, called the ethyl hydrogen sulfate route follows the following equation:

$$3C_2H_4 + 2H_2SO_4 \longrightarrow C_2H_5HSO_4 + (C_2H_5)_2SO_4$$

$$C_2H_5HSO_4 + (C_2H_5)_2SO_4 + 3H_2O \longrightarrow 3C_2H_5OH + 3H_2SO_4$$

Ethyl ether is a by-product.

The second is the Shell or direct hydration process and involves the temperature and pressure hydration over a phosphoric acid catalyst:

$$C_2H_4 + H_2O \longrightarrow C_2H_5OH$$

Waste Sources

The ethyl hydrogen sulfate has numerous waste sources. These include slops from the recovery and reconcentration of sulfuric acid (0.05 lb/lb of product) and the discharge of a caustic waste stream containing alcohol, ether and waste products from the alcohol scrubber. This stream may amount to several hundred gallons per ton of product and contain 1-3,000 mg/l of COD at a high pH (11). An additional stream results from the recycling column which removes the heavy ends, and is an aqueous stream of perhaps 10-30 gals/ton of product and contains about 5,000 mg/l of COD.

The direct hydration process involves considerably less waste. The major stream would result from the separation of the product ethanol from the process bottoms and may amount to 30-60 pounds of COD/ton of product.

Waste Reduction Through Process Change

It is possible to minimize the waste products by careful control of the use of sulfuric acid in the process and as is often the case, in the use of acid and alkali, the avoidance of leaks and spills. Additional stripping capacity and improved yields would also reduce waste product loads.

ETHYL BENZENE AND STYRENE

Producers (Styrene)	Capacity*
Amoco, Texas City, Texas	300
Cosden, Big Spring, Texas	100
Cos-Mar, Carville, La.	500
Dow, Freeport, Texas	550
Dow, Midland, Michigan	350
El Paso, Odessa, Texas	120
Enjay, Baytown, Texas	150
Foster Grant, Baton Rouge, La.	200
Marbon, Baytown, Texas	125
Monsanto, Alvin, Texas	40
Monsanto, Texas City, Texas	750
Shell, Torrance, Calif.	240
Sinclair-Koppers, Houston, Texas	70
Sinclair-Koppers, Kobuta, Pa.	270

*millions of pounds annually

Producers (Styrene)	Capacity*
Sinclair-Koppers, Port Arthur, Texas	150
Signal, Houston, Texas	35
Sunray DX, Corpus Christi, Texas	80
Suntide, Corpus Christi, Texas	75
Tenneco, Chalmette, La.	22
Union Carbide, Institute, W. Va.	130
Union Carbide, Seadrift, Texas	300
Total	3,991

*millions of pounds annually

Producers (Styrene)	Capacity*
Sinclair-Koppers, Port Arthur, Texas	150
Signal, Houston, Texas	35
Sunray DX, Corpus Christi, Texas	80
Suntide, Corpus Christi, Texas	75
Tenneco, Chalmette, La.	22

Producers (Styrene)	Capacity*
Union Carbide, Institute, W. Va.	130
Union Carbide, Seadrift, Texas	300
Total	3,991

*millions of pounds annually

Production (Styrene)

1968: 3.5 billion pounds
1973: 5.0 billion pounds

Uses

Polystyrene, Rubber modified polystyrene, Styrene-butadiene copolymer, ABS, SAN plastics, Styrene-butadiene elastomer

Processes

About 10 percent of the ethyl benzene is obtained by fractionation of petroleum streams. The dominant route is via alkylation of benzene with ethylene. It is expected to continue in this fashion in the future. There are two alternative routes to ethyl benzene by alkylation. One involves the use of high purity ethylene while the other involves the use of low concentration ethylene. It is expected that the latter will become more prominent in the future.

Styrene is produced from ethyl benzene by the high temperature dehydrogenation of the ethyl benzene.

Waste Problems

A number of waste streams arise from the alkylation of benzene with high concentration ethylene. Among these are the caustic and water washing streams used to wash the crude alkylate which contain 5-10,000 mg/l of tars and other polymers together with significant amounts of ethyl benzene and benzene. The overheads from the benzene drying column may contain minor amounts of benzene. The residue from the PEB (polyethyl benzenes) column contain tars and polymers formed during the process. The total organic burden is in the order of 30-70 pounds/ton of product.

The process utilizing low concentration ethylene produces primarily a waste stream containing polymers and tars and amounts to 50-100 pounds of organics per ton of product.

The styrene producing process condenses a water-styrene-ethyl benzene mixture and the water leaving this step contains oils as well as ethyl benzene and styrene.

Waste Reduction Through Process Change

Design of gas washers which improve contact conditions is one key to the reduction of wastewaters coming from this process (high concentration). A larger benzene drying column will reduce benzene losses from this system. The tars and polymers produced from the final separator could be incinerated rather than sent to a wastewater system.

ETHYLENE DICHLORIDE, VINYL CHLORIDE AND POLYVINYL CHLORIDE

Producers (Vinyl chloride)	Capacity*
Allied, Moundsville, W. Va.	500
American Chemical, Watson, Calif.	170
Conoco-Stauffer, Lake Charles, La.	600
Cumberland Calvert, Calvert City, Ky.	100
Diamond, Deer Park, Texas	100
Dow, Freeport, Texas; Plaquemine, La.	1,000
Ethyl, Baton Rouge, La.; Houston, Texas	300
General Tire, Ashtabula, Ohio	75
Goodrich, Calvert City, Ky.	800
Goodrich, Niagara Falls, N. Y.	40
Goodyear, Niagara Falls, N. Y.	70
Monochem, Geismer, La.	250
PPG, Lake Charles, La.	300
Tenneco, Houston, Texas	200
Union Carbide, S. Charleston, W. Va.	340
Union Carbide, Texas City, Texas	
Wyandotte, Geismer, La.	150
Total	5,150

*millions of pounds per year

Production

1968: 2.7 billion pounds
1973: 4.0 billion pounds

Uses

PVC

Processes

There are several major routes to vinylchloride. Acetylene based processes employ the use of hydrogen chloride in a direct addition in acetylene.

$$C_2H_2 + HCl \longrightarrow C_2H_3Cl$$

Ethylene processes involve direct chlorination plus dehydro chlorination

$$C_2H_4 + Cl \longrightarrow C_2H_4Cl_2 \text{ (ethylene dichloride)}$$

$$C_2H_4Cl_2 \longrightarrow C_2H_3Cl + HCl$$

A newer approach involves oxychlorination and permits the reuse of the HCl generated during dehydro chlorination (Copper chloride is the catalyst.).

$$C_2H_4 + 1/2\,O_2 + 2HCl \longrightarrow C_2H_4Cl_2 + H_2O$$

It is expected that all vinyl chloride in the country will be produced by a balanced chlorination-oxychlorination approach in the future.

Polyvinyl chloride is polymerized directly from vinyl chloride using different approaches.

Waste Problems

The vinyl chloride facility generates a waste stream containing about eight gallons/ton of product and containing minor amounts of organics (0.01 lbs/ton) with significant amounts of NaCl, $FeCl_3$, NaOH , and $NaClO_3$.

The waste stream from the PVC operation is about 2,000 gallons/ton of product and has a COD of 1,200-1,400 mg/l.

Waste Reduction Through Process Change

The advent of oxychlorination has made a major reduction in waste problems in the production of vinyl chloride. Waste problems are quite minor and little promise of change exists. Only minor pressure exists for the reduction in waste loadings from the PVC operation although changes in polymerization techniques may effect changes.

ETHYLENE

Producers	Capacity*
Allied-Wyandotte, Geismar, La.	500
American Can-Skelly, Clinton, Iowa	400
Atlantic, Watson, Calif.	100
Continental Oil, Lake Charles, La.	400
Dow, various locations	1,920
DuPont, Orange, Texas	800
El Paso-Rexall, Odessa, Texas	290

Producers	Capacity*
Enjay, various locations	1,265
Goodrich, Calvert City, Ky.	250
Gulf, various locations	825
Jefferson, Port Neches, Texas	450
Koppers, Kobuta, Pa.	35
Mobil, Beaumont, Texas	450
Monsanto, various locations	750
National Distillers, Tuscola, Illinois	320
Olin-Mathieson, Brandenburg, Ky.	90
Petroleum Chemicals, Lake Charles, La.	360
Phillips, Sweeny, Texas	550
Phillips-Houston Natural Gas, Sweeney, Texas	550
Shell, various locations	845
Sinclair-Koppers, Houston, Texas	500
Sun Olin, N. Claymount, Del.	125
Texas Eastman, Longview, Texas	450
Union Carbide, various locations	3,975
Total	16,000

*millions of pounds per year

Production

1968: 12,500,000,000 pounds per year
1973: 19,000,000,000 pounds per year

Uses

Polyethylene, ethylene oxide, ethanol, styrene, vinylchloride

Processes

Ethylene is produced from ethane and propane, refinery off-gas and other sources such as naphtha, gas oil, condensate. The first step involves cracking, then compression followed by purification. Ethylene production is an important source of propylene, butadiene, and aromatics.

Waste Problems

The major waste streams are

1) blowdown from steam cracking,
2) coke and tar in the furnace,
3) compressor water (oily),
4) spent caustic from acid gas scrubbing,
5) water from dryers,
6) green oil produced as a polymerization product during acetylene hydrogenation, and

g) acidic pH from thermal cracking step.

Typical quantities are:

Spent caustic - 15 gallons/ton of product containing 2.5 percent NaOH, 1.0 percent Na_2S and 6.6 percent ppm of phenols and 1,000 to 2,000 mg/l of COD.

Waste Reduction by Process Change

The process condensate stream may be reprocessed by being sent to a stripper and stripped by live steam. This will strip most of the non-phenol contaminants and about 20-25 percent of phenol. If fresh feed is contacted with the process condensate, it is possible to strip out most of the phenol which is then sent with the feed to the cracking furnace. The phenol free wastewater can then be steam stripped to remove residual volatile hydrocarbons. The water stream, free of contaminants may be reused in steam generation in the plant.

Studies are underway to recover the alkali from the spent caustic. For the moment, sulfide oxidation is generally practiced to reduce the immediate oxygen demand of this stream.

Green oil is piped to plant fuel systems or incinerators and burnt along with tar and other heavy polymer by-products.

ETHYLENE OXIDE

Producers (Ethylene Oxide)	Capacity*
Allied, Orange, Texas	40
Calcasieu, Lake Charles, La.	150
Dow, various locations	900
DuPont	300
Eastman, Longview, Texas	60
GAF, Linden, N. J.	70
Houston Chemical	80
Jefferson, Port Neches, Texas	50
Olin-Mathieson, Brandenburg, Ky.	120
Shell Chemical, Norco, La.	150
Sun Olin, Marcus Hook, Pa.	100
Union Carbide, various locations	1,700
Wyandotte, Geismer, La.	100
Total	4,520

*millions of pounds per year

Production

1968: 3,000,000,000 pounds/year (Ethylene Oxide)
1973: 5,000,000,000 pounds/year

Use

Surfactants, ethanol amines, polyglycols, anti-freeze, polyester fibers

Processes

The chlorohydrin method involves the reaction of chlorine water with ethylene to produce the chlorohydrin and HCl. This was then treated with bicarbonate to produce the glycol:

$$C_2H_4 + Cl_2 + H_2O \longrightarrow CH_2OH - CH_2Cl + HCl$$

$$CH_2OH - CH_2Cl + H_2O\ NaHCO_3 \longrightarrow CH_2OH - CH_2OH + NaCl + H_2CO_3$$

Ethylene oxide could be produced by adding caustic and rectifying the vapors.

Direct oxidation of ethylene:

$$C_2H_4 + 1/2\ O_2 \longrightarrow C_2H_4O$$

is the process which is now widely practiced. Hydrolysis of the oxide produces the glycol. The product of various glycol ethers and glycols as by-products is quite common.

Waste Problems

The older chlorohydrin process produces great quantites of waste HCl (which is usually lime neutralized) as well as waste organic streams. The major waste stream is a lime slurry (about 2,000 gallons/ton). It is not expected that any chlorohydrin plants will be built in the future.

Oxidation-hydration plants produce two major waste streams. One is produced at the rate of 1,500 gallons/ton of product and contains 0.1 percent organic. The other is produced at the rate of 150 gallons/ton of product and contains one percent organics in the process. In a similar system, the total water flow was about 1,000 gallons/ton of product with a concentration of 1-20,000 mg/l COD. Both contain a mixture of oxide, glycol, polyglycols, etc.

Waste Reduction Through Process Change

It is possible through the addition of stripping columns and the addition of certain streams to cooling water systems to reduce the wastewater discharge to 10 percent of the numbers cited above. The cost is in the order of $150-210,000 in a 50,000,000 pounds/year plant.

ISOPROPYL ALCOHOL

Producers	Capacity*
Enjay, Baton Rouge, La.	680
Shell, Dominguez, Calif.	225
Shell, Houston, Texas	380
Union Carbide, Texas City, Texas	400
Union Carbide, Whiting, Indiana	275
Total	1,960

*millions of pounds per year

Production

1968: 1,750 million pounds
1973: 2,250 million pounds

Uses

Acetone, solvent

Processes

Isopropyl alcohol is manufactured either by catalytic hydration of propylene:

$$CH_3 - CH = CH_2 + H_2O \longrightarrow CH_3CHOHCH_3$$

or by the reaction of sulfuric acid-propylene similar to the ethanol reaction.

Waste Problems and Process Change

See Ethanol

FORMALDEHYDE

Producers	Capacity*
Allied	310
Borden	925
Celanese	950
Commercial Solvents	60
DuPont	900
GAF	100
Georgia Pacific	120
Gulf	115
Hercules	275
Hooker	90
Monsanto	400

Producers	Capacity*
Reichhold	212
Rohm and Haas	50
Tenneco	325
Trojan Powder	50
Union Carbide	150
Total	5,042

*millions of pounds per year

Production

1968: 4.0 billion pounds
1973: 5.2 billion pounds

Uses

Phenolic resins, urea and melamine resins, ethylene glycol.

Process

Straight oxidation of methanol with air or oxygen. The major by-products are dimethyl ether and formic acid which amount to 150 pounds/ton of product.

Waste Problems

The major sources of waste are the scrubber waters and the dimethyl ether by-product. The total aqueous stream should not exceed 100 gallons/ton containing 1-5,000 mg/l COD unless truck washing is practiced at the site.

METHANOL

Producers	Capacity*
Allied	26
Borden	160
Celanese	75
CSC	65
DuPont	380
Escambia	30
Gulf	9
Hercules	16
Monsanto-Tenneco	30
Rohm and Haas	22
Tenneco	76
Union Carbide	64
Total	943

*millions of gallons per year

Production

1968: 600 million gallons
1973: 900 million gallons

Uses

Formaldehyde, methyl esters, amines, solvent

Processes

The major process for the production of methanol involves the high pressure catalytic conversion of synthesis gas ($CO + H_2$) to methanol. Recently ICI has developed a low pressure process.

Waste Problems

Although little information is available on the lower pressure process, only minor differences between waste streams would appear to exist. Major wastewater streams are from slab and vessel wash downs together with bottoms from the methanol purification process. This amounts to 100-500 gallons/ton of product and contains some oils, methanol and higher boiling organics to the extent of several hundred mg/l.

Waste Reduction Through Process Change

More effective separations and better housekeeping can produce greatly reduced water flows. The dimethyl ether produced from this waste can be sent to a formaldehyde production facility for conversion into formaldehyde.

PHENOL

Producers	Capacity*
Allied	350
Chevron	50
Clark Oil	50
Dow	270
Hercules	50
Hooker	130
Monsanto	285
Reichhold	90
Shell	50
Skelly Oil	50
Union Carbide	575
Total	1,950

*million pounds per year

Production

1968: 1,500 million pounds
1973: 2,200 million pounds

Uses

Phenolic resins, caprolactam, bisphenol-A, adipic acid

Processes

Phenol is made from benzene by the Raschig process

$$C_6H_6 + HCl + 1/2\,O_2 \longrightarrow C_6H_5Cl + H_2O$$

$$C_6H_5Cl + H_2O \longrightarrow C_6H_5OH + HCl$$

from benzene by the chlorobenzene route:

$$C_6H_6 + Cl_2 \longrightarrow C_6H_5Cl + HCl$$

$$C_6H_5Cl + 2NaOH \longrightarrow C_6H_5ONa + NaCl + H_2O$$

$$C_6H_5ONa + HCl \longrightarrow C_6H_5OH + NaCl$$

and by the sulfonation process from benzene:

$$C_6H_6 + H_2SO_4 \longrightarrow C_6H_5SO_3H + H_2O$$

$$2C_6H_5SO_3H + Na_2SO_3 \longrightarrow 2C_6H_5SO_3Na + SO_2 + H_2O(+Na_2SO_4)$$

$$C_6H_5SO_3Na + 2NaOH \longrightarrow C_6H_5ONa + Na_2SO_3 + H_2O$$

$$2C_6H_5ONa + SO_2 + H_2O \longrightarrow 2C_6H_5OH + Na_2SO_3\ (+Na_2SO_4)$$

Recently two new routes have been commercialized. One is the Dow Chemical process which involves direct oxidation of toluene to benzoic acid and then oxidation of the benzoic acid to phenol in a single step.

It is anticipated that cumene based phenol will continue to hold a major share of the market. Furthermore, it is expected that the direct oxidation routes will also gain importance.

Waste Problems

In addition to quantities of wastewaters discharged from the separation of the phenol the less used processes all produce major quantities of inorganic containing aqueous wastes which create considerable difficulties relative to waste treatment. A typical 100,000,000 pound/year phenol plant based on cumene produces a stream of 200,000 gpd of wastewater containing 13,200 mg/l of COD and 180 mg/l of phenol. Inorganics are produced at the following rates:

Sodium carbonate (5,000 lbs/day); sodium formate (500 lbs/day); sodium bicarbonate (500 lbs/day) and sodium sulfate (22,000 lbs/day)

The waste production from the direct oxidation facility might be considerably less than the older process.

Waste Reduction Through Process Control

It is possible to reduce effluents by careful control of the process involved, recovery of the inorganics by crystallization, etc., and by solvent extraction of the phenol. It is also likely that as the sulfonation and chlorination approaches are reduced in importance, the amount of waste generated per pound of phenol produced will be greatly reduced.

POLYETHYLENE - HD

Producers	Capacity*
Allied, Baton Rouge, La.	150
Allied, Orange, Texas	25
Celanese, Pasadena, Texas	150
Chemplex, Clinton, La.	50
Dow, Freeport, Texas	50
Dow, Plaquemine, La.	50
DuPont, Orange, Texas	75
Gulf, Orange, Texas	100
Hercules, Parlin, N. J.	80
Monsanto, Texas City, Texas	100
National Petrochemicals, La Porte, Texas	125
Phillips, Pasadena, Texas	160
Sinclair-Koppers, Port Reading, N. J.	50
Union Carbide, Seadrift, Texas	125
Total	1,280

*millions of pounds per year

Production

1968: 1,200 million pounds
1973: 2,000 million pounds

Uses

Blow molding, injection molding, film and sheet, wire and cable, pipe and conduit

Processes

Polyethylene is produced by the catalyzed polymerization of ethylene. High pressure processes use oxygen or peroxides as a catalyst while the low pressure processes (which produce high density products) use metal derived catalysts.

Waste Problems

About 400 gallons/ton of product of wastewater is produced from these units and this flow has the following characteristics:

Suspended Solids	100 ppm
COD	500-800 mg/1

Waste Reduction by Process Changes

It is possible to greatly reduce the discharge of solids by improving the utilization of centrifuges and other separation equipment.

POLYETHYLENE - LD

Producers	Capacity*
Allied, Orange, Texas	25
Chemplex, Clinton, Iowa	100
Columbian Carbon, Lake Charles, La.	100
Dow, Freeport, Texas	170
Dow, Plaquemine, La.	130
DuPont, Orange, Texas	425
DuPont, Victoria, Texas	200
Eastman, Longview, Texas	175
Enjay, Baton Rouge, La.	200
Gulf, Cedar Bayou, Texas	200
Gulf, Orange, Texas	200
Monsanto, Texas City, Texas	130
National Distillers, Deer Park, Texas	300
National Distillers, Tuscola, Illinois	150
Rexall-El Paso, Odessa, Texas	250
Sinclair-Koppers, Port Arthur, Texas	125
Union Carbide, Seadrift, Texas	200
Union Carbide, S. Charleston, W. Va.	100
Union Carbide, Taft, La.	500
Union Carbide, Texas City, Texas	290
Union Carbide, Torrance, Calif.	80
Union Carbide, Whiting, Indiana	200
Total	4,250

*millions of pounds per year

Production

1968: 2,900 million pounds
1973: 4,700 million pounds

Uses

Film and sheet, injection molding, extension coating, wire and cable

Processes

See Polyethylene-HD

Waste Problems

The waste stream which is primarily drains, amounts to 200 gpd/ton of product and contains 50-100 mg/l COD and 100 mg/l of oil.

Waste Reduction

See Polyethylene-HD

POLYSTYRENE

Producers	Capacity*
Amoco, Leominster, Mass; Medina, O; Torrance, Calif; Willow Sp., Ill.	120
Badische, Jamesburg, N. J.	25
Columbian, Hicksville, N. Y.	10
Cosden, Big Springs, Texas	120
Dow, Allyns Pt., Conn; Ironton, O; Midland, Mich; Torrance, Calif; Riverside, Mo.	610
Foster Grant, Leominster, Mass; Peru, Ill. Hammond, Worcester, Mass.	50
Monsanto, Addyston, O; Long Beach, Calif; Springfield, Mass.	300
Rexall, Holyoke, Mass; Santa Clara, Calif.	70
Richardson, West Haven, Conn.	30
Shell, Wallingford, Conn.	25
Sinclair-Koppers, Kobuta, Pa.	190
Solar, Leominster, Mass.	50
Union Carbide, Bound Brook, N. J.; Marietta, O.	165
Total	1,865

*millions pounds per year

Production

1968: 1.7 million tons
1973: 3.0 million tons

Uses

Molding, Blow extrusion

Processes

Polymerization with or without catalysts

Waste Problems

A typical plant produces a waste of 600 gallons/ton of product with the following composition:

Styrene	3 ppm
Benzoyl Peroxide	1,400 ppm
Tricalcium Phosphate	800 ppm Ca 2,200 ppm PO_4
Alkyl Aryl Sulfonate	80 ppm
Suspended Solids	500 ppm

PROPYLENE

Producers	Capacity*
Ashland, Catlettsburg, Ky.	130
Atlantic-Richfield, Watson, Calif.	230
Amoco, various locations	510
Chevron, El Segundo, Calif.	160
Cities Services, Lake Charles, La.	320
Clark, Blue Island, Ill.	70
Dow, various sites	440
DuPont, Orange, Texas	200
El Paso, Odessa, Texas	60
Enjay, various sites	1,440
Goodrich, Calvert City, Ky.	90
Gulf, various sites	830
Jefferson, Port Neches, Texas	150
Marathon, Texas City, Texas	70
Mobil, Beaumont, Texas	520
Monsanto, various sites	360
Petroleum Chemicals, Lake Charles, La.	60
Phillips, Sweeney, Texas	180
Shell, various sites	630
Signal, Houston, Texas	90
Sinclair, Houston, Texas & Marcus Hook, Pa.	380
Sinclair-Koppers, Houston, Texas	100
Skelly, El Dorado, Kansas	90
Sohio, Lima, Ohio	110
Sun, Marcus Hook, Pa.	300
Suntide, Corpus Christi, Texas	70
Texaco, Westville, N. J.	140

Producers

Producers	Capacity*
Texas City Ref., Texas City, Texas	100
Texas Eastman, Longview, Texas	100
Tidewater-Air Products, Delaware City, Del.	250
Union Carbide, various sites	550
Union Oil, Los Angeles, Calif.	140
Total	8,920

*millions of pounds per year

Production

1968: 7,000 million pounds per year
1973: 11,000 million pounds per year

Uses

Isopropanol, acrylonitrile, polypropylene, propylene oxide, heptene, cumene, glycerine

Processes

Propylene is produced together with ethylene and details may be obtained from the section on ethylene. However, the major portion of the propylene is produced as a by-product of gasoline product (over 85 percent). It is expected that the amount of propylene generated will increase as the demand for high octane low leaded gasolines increase.

Waste Reduction

See ethylene section

PROPYLENE OXIDE

Producers

Producers	Capacity*
Celanese, Bishop, Texas	10
Dow, Freeport, Texas	225
Dow, Midland, Mich.	25
Jefferson, Port Neches, Texas	120
Olin, Brandenburg, Ky.	80
Oxirane, Bayport, Texas	150
Union Carbide, S. Charleston, W. Va.	200
Wyandotte, Wyandotte, Mich.	160
Total	1,020

*millions of pounds per year

Production

1968: 890 million pounds
1973: 1,750 million pounds

Uses

Polypropoxyethers, propylene glycol, polypropylene glycol, dipropylene glycol

Process

See Ethylene Oxide section. Oxirane has developed a process based on the oxidation of acetaldehyde.

Waste

See Ethylene Oxide

TOLUENE

Producers	Capacity*
Amoco, Texas City, Texas	20
Ashland, North Tonawanda, N. Y., Catlettsburg, Ky.	20
Atlantic-Richland, Wilmington, Calif.	24
Chevron, El Segundo, Calif; Richmond, Calif.	32
Cities Services, Lake Charles, La.	36
Coastal States, Corpus Christi, Texas	10
Cosden, Big Spring, Texas	15
Crown Central, Houston, Texas	10
Dow, Bay City, Mich.	17
Enjay, Baton Rouge, La; Baytown, Texas	65
Gulf, Philadelphia, Pa; Port Arthur, Texas	20
Hess, Corpus Christi, Texas	18
Leonard, Mount Pleasant, Mich.	3
Marathon, Texas City, Texas	12
Mobil, Beaumont, Texas	25
Monsanto, Alvin, Texas	32
Pontiac, Corpus Christi, Texas	13
Shell, Houston, Texas; Odessa, Texas; Wilmington, Calif; Wood River, Ill.	65
Signal, Houston, Texas	16
Sinclair, Houston, Texas; Marcus Hook, Pa.	26
South Hampton, Silsbee, Texas	6
Southwester, Corpus Christi, Texas	10
Sun, Marcus Hook, Pa.	25
Sunray DX, Tulsa, Okla	4
Suntide, Corpus Christi, Texas	13
Tenneco, Chalmette, La.	8

Producers	Capacity*
Texaco, Port Arthur, Texas	31
Union Carbide, S. Charleston W. Va.	10
Union Oil-Atlantic, Nederland, Texas	20
Union Oil, Lemont, Ill.	10
Vickers, Potwin, Kansas	5
Total	620**

*millions of gallons per year

**also 65 million gallons from coke oven, tar distiller and styrene monomer operations

Production

1968: 610 million gallons
1973: 800 million gallons

Uses

Benzene, solvents, gasoline, TNT, Toluene diisocyanate, phenol

Process

Toluene is produced by extraction from refinery reformate as is benzene. For details see benzene.

UREA

Producers	Capacity*
Allied	320
American Cyanamid	150
Arkla	67
Armour	17
Best	20
Collier	50
Columbia Nitrogen	25
Cooperative Farmer	50
DuPont	205
Escambia	23
Farmers Chemical	30
Fel Tex	20
Grace	100
Gulf	90
Hawkeye	25
Hercules	60
Ketman	7
Miss. Chem.	80
Mobile	5

Producers	Capacity*
Monsanto	80
Nipack	260
Nitrin	23
Olin	150
Phillips	8
Phillips Pacific	20
Premier	70
Shell	185
Solar	140
Southern Nitrogen	60
Sun Olin	75
Valley Nitron	35
Wycon	50
Total	1,500

*thousands of tons

Production

1968: 2.3 million tons
1973: 3.7 million tons

Uses

Animal feed, fertilizer, plastics

Processes

All of the major processes involve the high pressure reaction of CO_2 and ammonia. There are about 10 variations of this scheme.

Waste Problems

Typical wastes amount to about 120 gallons/ton of product with the following composition:

	lbs/ton
NH_3	3.6
CO_2	0.6
Urea	0.8
Carbonate	0.1

Waste Reduction Through Process Change

It is normal practice to remove about 50 percent of the ammonia by airstripping after adjusting pH with alkali. Recently two new processes have been developed which strip the ammonia and carbonate by contacting with either NH_3 or CO_2 and sending the overload directly to the reactor. This approach is expected to reduce ammonia losses by 50 percent or more with a more drastic effect on carbonate. These also involve operation of the reaction at a lower temperature.

XYLENES

Producers	Ortho Capacity*	Para Capacity*
Amoco	-	200
Chevron	130	536
Cities Service	120	-
Coastal	42	6
Commonwealth	70	-
Cosden	-	6
Crown Central	19	-
Enjay	175	210
Hercor	-	100
Hess	45	-
Monsanto	75	-
Shell	-	100
Signal	-	15
Sinclair	80	215
Sunray DX	30	165
Tenneco	25	100
Total	736	1,547

*millions of gallons per year

Production

	Ortho	Para
1968	500	750
1973	750	1,800

Uses

Phthalic anhydride, polyesters

Process

Mixed xylenes are recovered primarily from refinery streams (see benzene and ethyl benzene). It is separated with ethyl benzene and isomerization is carried out to increase the yield of para xylene. A separation scheme involves crystallization to separate the various streams.

Waste Problems

Sludge from the crystallizer as well as bottoms, drains, etc., amount to perhaps 100-500 gallons/ton of product with an organic content of 3-5,000 mg/1.